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Hydrates in the Methane-Ethylene System

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

by

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HYDRATES IN THE METHANE-ETHYLENE SYSTEM

ABSTRACT

The initial hydrate forming conditions for the systems ethylene-water and methane-ethylene-water, have been extended to 5000 lb/in.² abs. It was found that at a given pressure, the initial hydrate forming temperature for mixtures containing greater than about 65 mole percent ethylene was higher than the initial formation temperature for either methane or ethylene.

A comparison between experimental and predicted hydrate forming conditions for the system methane-ethylene-propylene-water was made for three different mixtures of these gases. This comparison showed that the predicted hydrate forming temperature was slightly higher at a given pressure.

An attempt was made to obtain experimental solid-vapor equilibrium ratios for methane, ethylene and propylene using mixtures of methane and propylene, in the presence of water.

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List of Symbols

n	Number of moles
F	Number of degrees of freedom
C	Number of components
P	Pressure; in phase rule - number of phases
T	Temperature
V	Vapor
S	Solid hydrocarbon
I	Ice
L ₂	Hydrocarbon-rich liquid
L ₁	Water-rich liquid
H	Hydrate
K	Equilibrium ratio
y	Mole fraction of component in vapor phase
x	Mole fraction of component in liquid phase
z	Mole fraction of component in hydrate

I. INTRODUCTION

The significance of gas hydrate in industry was first realized by Hammerschmidt (4) in 1934 when he found that the plugging of valves and pipes was due to the formation of the C_1 - C_4 hydrocarbon hydrates. These hydrates form according to the equation:



where R is the hydrocarbon molecule and n is the number of water molecules.

The value of n has been determined for a number of gases by Claussen (2) using the x-ray technique of von Stackelberg and Muller (8). For methane, the value of n was found to be 6.3 and for the larger molecule of ethylene the value is 7.4.

Hydrates have been investigated in the C_1 - C_4 paraffinic and olefinic hydrocarbons. It is not believed that pentane and the higher hydrocarbons will form hydrate, but this has not been proven.

The usual method to avoid hydrate formation is by dehydration of the gas. Moreau (5) found that addition of glycol to the gas stream from a well inhibits hydrate formation by combining with any free water in the tubing. This will not work however, if the well is producing formation water. Numerous other methods for preventing hydrate formation have been tried but from a practical standpoint, the trouble incident to hydrate formation has only been solved by dehydration of the gas before it enters the plant or pipe line.

A correlation for the prediction of hydrate formation has been presented for methane by Katz (1) using vapor-solid equilibrium ratios.

Based upon the correlation of Katz for methane, Otto (6) obtained vapor-solid equilibrium ratios for ethylene and propylene.

This report describes an investigation to obtain vapor-solid equilibrium ratios for methane, ethylene and propylene. The incipient hydrate formation conditions for the systems ethylene-water and methane-ethylene-water were investigated to 5000 lb/in.²abs.

II PREVIOUS WORK

The hydrate of chlorine and water was the first known hydrate and was discovered by Humphrey Davy in 1810. The hydrate of acetylene and hydrogen sulfide was investigated but the first significant amount of work was done during 1880 - 1900, when Villard (9) made an extensive study of gas hydrates. He found the hydrate decomposition curves for methane, ethane and ethylene hydrates. No further work on hydrates was done until 1934 when Hammerschmidt (4) found that the plugging of valves and pipes in natural gas transmission lines was due to the formation of hydrates. He obtained hydrate forming conditions for a number of natural gases and investigated methods of preventing their formation.

Wilcox, Carson and Katz (10, 1) in 1941 proposed a method of predicting hydrate formation in natural gas by the use of solid-vapor equilibrium ratios. Carson and Katz (1) investigated hydrate forming conditions for methane-propane-water, methane-pentane-water and methane-hexane-water systems. They could not find any indication of hydrates in the methane-pentane-water or methane-hexane-water systems. Solid-vapor equilibrium ratios were also determined for methane and propane.

Otto (6) calculated solid-vapor equilibrium ratios for ethylene and propylene using Katz's equilibrium ratios for methane.

In 1951, Claussen (2) using the x-ray technique of M. v. Stackelberg and H. R. Muller, substantiated his earlier proposed crystal structure of hydrates. He found that there are two structures possible, depending on the size of the hydrocarbon molecule. Claussen also determined the value of n (number of molecules of water per molecule of hydrocarbon in hydrate) for a number of gases. These values are shown in Table I.

(1) Ethylene-Water System

The first person to experimentally investigate the ethylene-water system was Villard (9). He investigated the 3-phase equilibria, water-rich liquid, hydrate and vapor at a temperature of 63°F and for pressures to 867 lb/in.²abs. Diepen and Scheffer (3) investigated the three-phase equilibria, hydrate, vapor, ice and water-rich liquid, hydrate and vapor at a temperature of 64.4°F and for pressures to 793 lb/in.²abs. Reamer, Selleck and Sage (7) reported some data for the ethylene-water system but their data are scattered. Otto (6) determined the hydrate decomposition curve for the three-phase equilibria, water-rich liquid, hydrate and vapor up to 1963 lb/in.²abs. and 68.3°F.

The experimental results of Diepen and Scheffer and of Otto are presented in Table II.

(2) Methane-Ethylene-Water System

Otto was the first investigator to report data on the system CH₄-C₂H₄-H₂O. He determined hydrate forming conditions for the three-phase equilibria, water-rich liquid, hydrate and vapor, for eight mixtures of the two gases from 0 - 100 percent ethylene and pressures to approximately 1900 lb/in.²abs. The experimental data which he obtained for these systems are presented in Table III.

(3) Methane-Ethylene-Propylene-Water System

Otto (6) investigated the hydrate forming conditions for the three-phase equilibria for one mixture of this system. He then predicted the hydrate forming conditions using Katz's solid-vapor equilibrium

TABLE IVALUE OF n (number of molecules of water per molecule of gas)

W. F. CLAUSSEN (2)

Small Molecules
(filling all holes)Medium Sized Molecules
(filling only medium holes)Ar 4.5 H₂OC₂H₆ 7 H₂OCH₄ 6.3 H₂OC₂H₄ 7.4 H₂OC₂H₂ 5.7 H₂OC₂H₅F 8.27 H₂OPH₃ 5.9 H₂OSO₂ 8 H₂OH₂S 5.7 H₂OCH₃Cl 7.2 H₂OCO₂ 6 H₂OCl₂ 6.91 H₂ON₂O 6 H₂OBr₂ 10 H₂OH₂Se 5.87 H₂O

TABLE II

PREVIOUS WORK ON CONDITIONS FOR FORMATION OF ETHYLENE HYDRATE

3 PHASE EQUILIBRIA (liquid water-hydrate-vapor)

DIEPEN and SCHEFFER (3)

<u>P(psia)</u>	<u>T(°F)</u>
81.5	32.0
82.4	32.4
83.9	32.7
87.4	33.1
87.6	33.4
91.4	34.2
93.3	34.5
95.6	34.9
99.4	35.6
103	36.1
106	36.7
113.5	37.8
113	37.8
131	39.9
150	41.7
174	44.1
218	47.7
288	51.8
364	54.9
435	57.6
498	59.5
586	61.5
642	62.4
713	63.6
793	64.4

OTTO (6)

<u>P(psia)</u>	<u>T(°F)</u>
96	34.7
143	40.7
201	46.1
306	52.1
411	56.1
525	59.5
641	62.0
656	62.3
690	62.9
759	63.6
772	63.6
809	63.7
867	64.0
875	64.0
906	64.5
937	64.6
1004	64.3
1019	64.6
1090	64.8
1244	65.4
1277	65.7
1452	66.2
1474	66.4
1677	67.5
1811	67.4
1963	68.3

ratios for methane and his own calculated values for ethylene and propylene. The experimental and predicted curves were compared and an error of approximately 24% in the pressures was found, with the predicted value being lower at a given temperature. Otto's data for this system are presented in Table IV.

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TABLE III

PREVIOUS DATA FOR THREE-PHASE EQUILIBRIUM, H-L₁-V,IN THE CH₄-C₂H₄-H₂O SYSTEM BY OTTO (6)

Temperature °F	Pressure lb/in ² abs.	Mole % C ₂ H ₄ in Vapor (Dry Basis)	Mole % CH ₄ in Vapor (Dry Basis)
56.8	1487	2.8	97.2
49.1	879	2.8	97.2
35.0	388	2.9	97.1
59.8	1485	7.6	92.4
52.7	911	7.7	92.3
35.6	334	7.7	92.3
62.8	1474	17.4	82.6
58.0	1035	17.2	82.8
50.3	590	17.2	82.8
38.7	289	17.2	82.8
66.7	1484	33.7	66.3
55.8	624	33.7	66.3
67.7	1467	45.3	54.7
63.2	944	45.0	55.0
56.0	555	44.8	55.2
38.2	183	44.9	55.1
71.3	1939	66.3	33.7
68.5	1300	65.8	34.2
64.0	803	65.8	34.2
51.6	320	65.7	34.3
69.7	1951	90.3	9.7
66.8	1101	90.0	10.0
63.7	732	89.9	10.1
53.2	320	89.8	10.2
69.3	1959	96.6	3.4
65.4	988	96.7	3.3

TABLE IV

EXPERIMENTAL and CALCULATED HYDRATE FORMATION
 CONDITIONS BY OTTO (6)

Gas Composition: 64.8 mole % CH₄
 31.7 mole % C₂H₄
 3.5 mole % C₃H₆

<u>Temperature</u> <u>°F</u>	<u>Hydrate Formation Pressure</u> <u>lb/in² abs.</u>		<u>Percent</u> <u>Deviation</u>
	<u>Calculated</u>	<u>Experimental</u>	
66.9	1398	1941	28.0
65.1	1178	1533	23.1
61.0	790	1044	24.3
60.9	-	1031	-
58.6	654	831	21.3
48.9	341	430	20.7

III THEORY

Phase diagrams, the conventional method of representing phase equilibria, may be used to represent the hydrate forming conditions for hydrocarbon-water systems. The number of degrees of freedom which must be specified for this equilibrium is found from the phase rule which states, that if a heterogeneous system consisting of C components in P phases is in equilibrium then

$$F = C - P + 2$$

The variables to be considered in the use of this equation are pressure, temperature and composition. When there are zero degrees of freedom none of the above variables can be arbitrarily specified, one degree of freedom, either the pressure or temperature may be specified and for two degrees of freedom, two of either the pressure, temperature or composition may be specified.

Phase equilibria may be terminated in one of three ways:

1. by addition of another phase to the system. This can occur when the gas is below the critical conditions and a hydrocarbon liquid is able to form,
2. loss of a component. During hydration the liquid water, or liquid hydrocarbon or vapor may be completely used and thus the system loses a component, or,
3. by the reaching of a critical point where two phases become identical.

(1) Two Component System

Two component systems consist of a single hydrocarbon in the presence of water. The phase rule states that when three phases are

in equilibrium with two components, there is one degree of freedom. This means that the three-phase equilibria will be represented by a line on a phase diagram. When there are only two phases present, the phase rule gives two degrees of freedom and the two-phase equilibria will be represented as an area on the phase diagram. Two types of two component equilibria are possible depending on whether the hydrocarbon is above or below its critical point. Figure 1 is a representative phase diagram for the hydrocarbon above its critical, and Figure 2 for the hydrocarbon below its critical conditions. The methane-water and the ethylene-water systems are of the first type while the propane-water and propylene-water systems are of the second type.

On Figure 1, the line AB represents the three-phase equilibria, water-rich liquid, hydrate and vapor. This line gives the hydrate formation or decomposition condition for the system. Line AD, is the water-rich liquid freezing point line for the equilibria, liquid, vapor and ice. Line AC, represents the equilibria hydrate, vapor and ice. Point A is the triple point and is approximately at 32°F since relatively little hydrocarbon is dissolved in the liquid. Hydrate exists in the whole region to the left of CAB. If there is just the exact amount of hydrocarbon vapor and aqueous liquid to form the hydrate, no other phase will exist to the left of CAB. As usually is the case, however, hydrocarbon vapor will be in excess and vapor will exist with the hydrate to the left of CAB. If there is water in excess, ice and hydrate will exist together to the left of EA and above CA, and hydrate and aqueous liquid will exist to the right of EA and above AB.

On Figure 2, where the hydrocarbon is below its critical condition, line AB represents the three-phase equilibria L_1HV , line AD represents the

L_1VI , equilibria and line CA represents the HVI equilibria. As the pressure and temperature along line AB is increased, a point will be reached where a hydrocarbon-rich liquid forms. This adds another phase and according to the phase rule for two components in four-phase equilibria, there will be zero degrees of freedom. This means that there will be an invariant four-phase point on the phase diagram. This point is called a quadruple point and is the four-phase equilibria between water-rich liquid, hydrocarbon-rich liquid, hydrate and vapor. Line BF represents the three-phase equilibria, L_1L_2V , line BG is the L_1L_2H equilibria, line BJ represents the L_2HV equilibria if there is excess hydrocarbon. This line can also represent the metastable L_1L_2V equilibria. If there is hydrocarbon in excess, hydrate and vapor will exist to the left of CAB and below BJ and hydrocarbon-rich liquid and hydrate will exist to the left of BG and above BJ. If aqueous liquid is in excess, hydrate and liquid water will exist to the right of EA and to the left of ABG, and hydrate and ice will exist to the left of EA and above AC.

(2) Three Component System

According to the phase rule for three component equilibria, i.e., a two component gas and water, there are two degrees of freedom for three phases in equilibrium. This means that in order to specify the remaining variables in the system, two of the variables, pressure, temperature and composition must be fixed. When there are two degrees of freedom, and assuming that the hydrate is a solid solution, it will melt over a range of temperature at a given constant pressure. Only when there is the four-phase L_1L_2HV equilibria will the system exhibit one degree of freedom and melt at a given temperature for a given pressure.

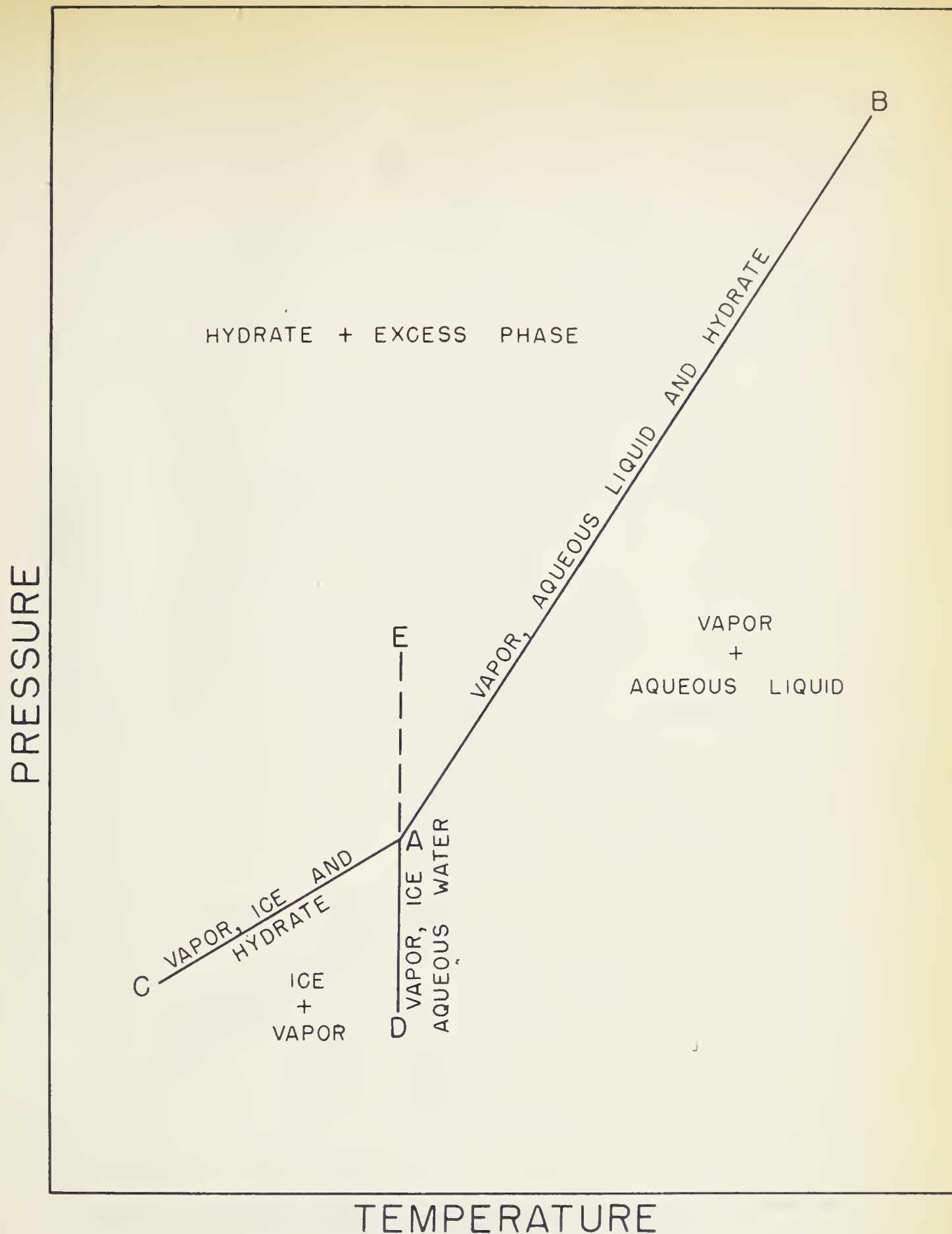


FIG. 1. HYDRATE EQUILIBRIA FOR BINARY HYDRO-CARBON—WATER SYSTEM WHERE SYSTEM IS ABOVE CRITICAL TEMPERATURE OF HYDROCARBON

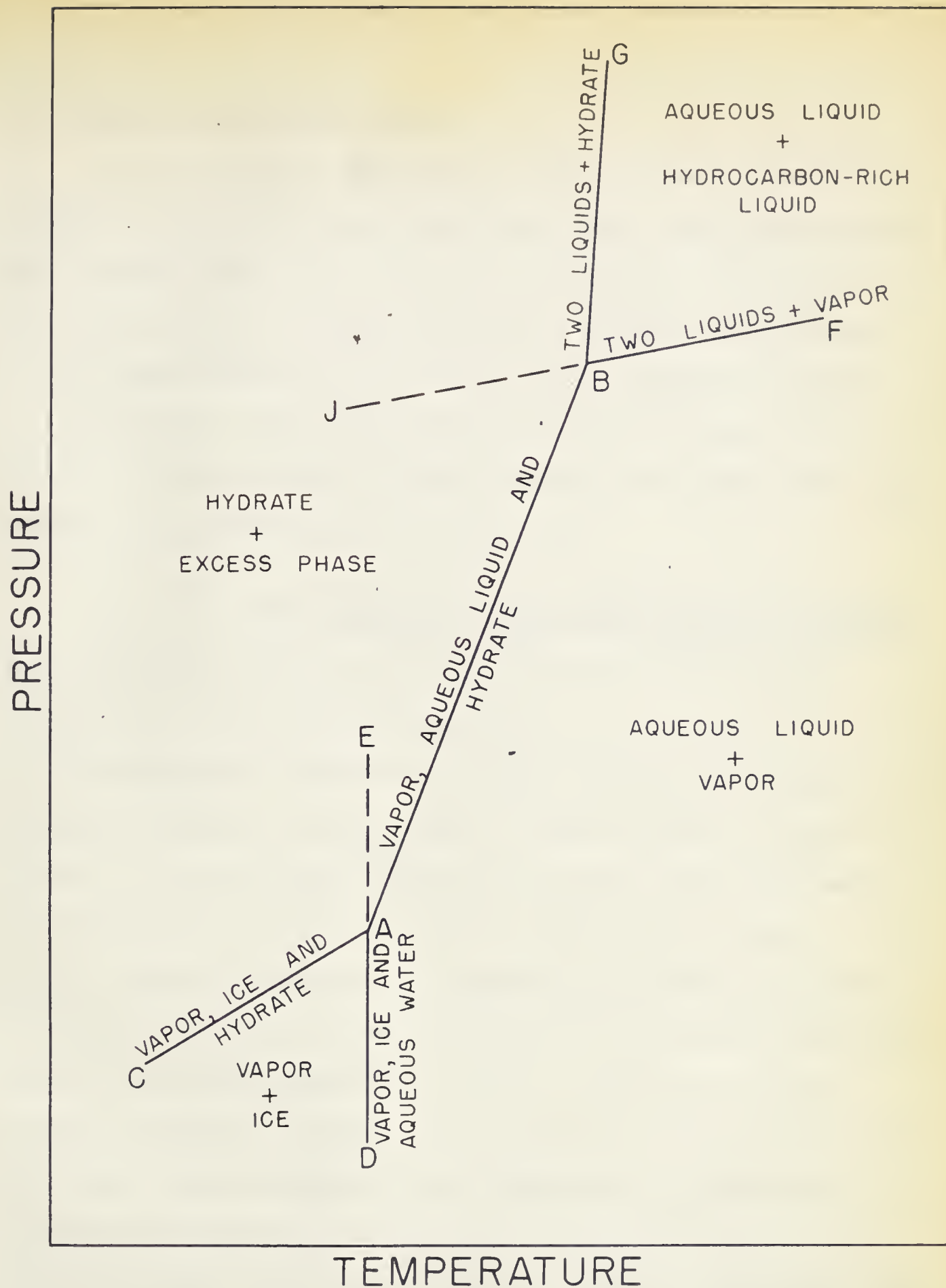


FIG. 2. HYDRATE EQUILIBRIA FOR BINARY HYDROCARBON—WATER SYSTEM WHERE SYSTEM IS BELOW CRITICAL TEMPERATURE OF HYDROCARBON

(3) Solid-Vapor Equilibrium Ratios

A useful method of predicting the hydrate forming conditions is through the use of solid-vapor equilibrium ratios. This method supposes that the solid-vapor equilibrium ratio is analogous to the liquid-vapor equilibrium ratio if the hydrates form solid solutions in each other. Wilcox, Carson and Katz (10, 1) were the first to apply this concept to a natural gas. These solid-vapor equilibrium ratios have proven adequate for the prediction of hydrate formation in a natural gas. They defined the solid-vapor equilibrium ratio as:

$$K_{v-s} = \frac{y}{z} = \frac{\text{mole fraction of a hydrocarbon in vapor (dry basis)}}{\text{mole fraction of a hydrocarbon in hydrate (dry basis)}}$$

These solid-vapor equilibrium ratios consider only the hydrocarbon portion of the vapor and solid phases.

Carson and Katz extended this concept to the determination of equilibrium constants for pure methane. These constants are shown in Figure 3. To obtain these constants three sources of data were used. They knew that for the hydrate formation point of pure methane, $K_{v-s} = 1$. They collected hydrate composition data they had determined at various pressures up to 1000 lb/in.²abs. for the four-phase equilibria L_1L_2HV on the methane-propane-water system. Then assuming that the presence of water had no effect on the liquid-vapor equilibrium for the hydrocarbon, they determined the vapor compositions for the methane-propane-water system at the pressures and temperatures that the hydrate equilibria existed. This gave them both the vapor and solid compositions and thus the K-value for a range of pressures. They obtained one point

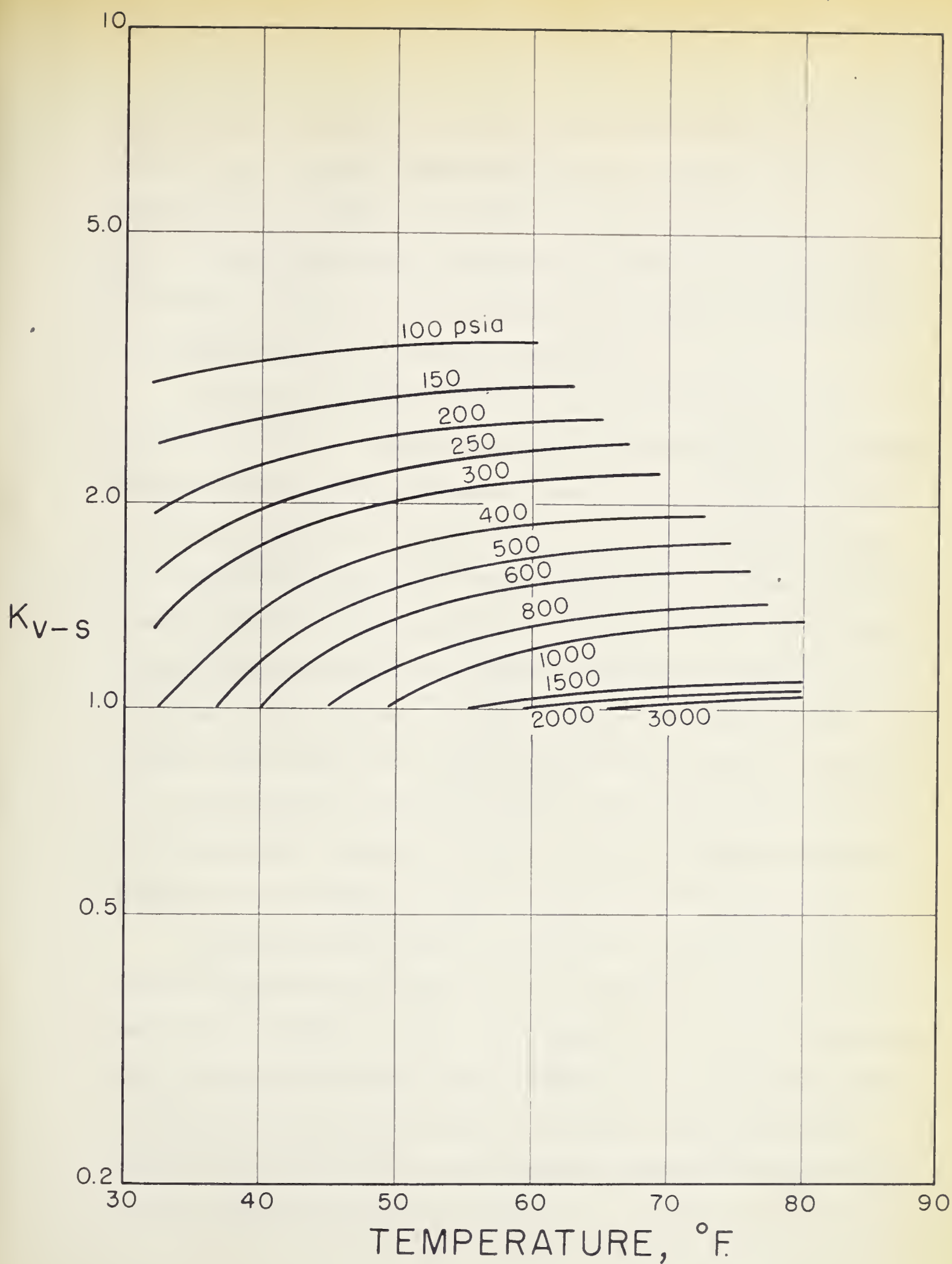


FIG. 3. SOLID-VAPOR EQUILIBRIUM RATIOS FOR METHANE (I)



from data Hammerschmidt had reported on the composition of a pipe line gas and a gas resulting from decomposition of a hydrate formed at 600 lb/in.²abs., giving K for methane at this pressure.

Using these points, the K curve for methane at 600 lb/in.²abs. was drawn, and curves for other pressures were drawn in symmetrically and extrapolated over the range of temperature.

To obtain equilibrium constants for other gases it is not necessary to obtain experimental hydrate composition data. If the vapor composition for a binary hydrocarbon-water system containing methane is known at the pressure and temperature at which the hydrate forms, the relationship $\sum \frac{y}{K}$ must equal unity at this point. Carson and Katz used this method to obtain K charts for ethane, propane and isobutane. Otto (6) calculated solid-vapor equilibrium ratios for ethylene and propylene by first finding the hydrate forming conditions for the methane-ethylene-water and methane-propylene-water systems. Knowing the vapor composition of these mixtures at the hydrate forming point, he was then able to construct K charts for the two olefin hydrocarbon hydrates. These charts are shown as Figures 4 and 5 respectively.

In the use of the equilibrium constants to calculate hydrate formation conditions for some pressure, assumptions are made as to the temperature until $\sum \frac{y}{K} = 1$ for all the components. Carson and Katz found that all components heavier than the butanes, including nitrogen, have a solid-vapor equilibrium constant of infinity, since they are not known to form hydrates. They also obtained equilibrium constants for the main components in a natural gas.

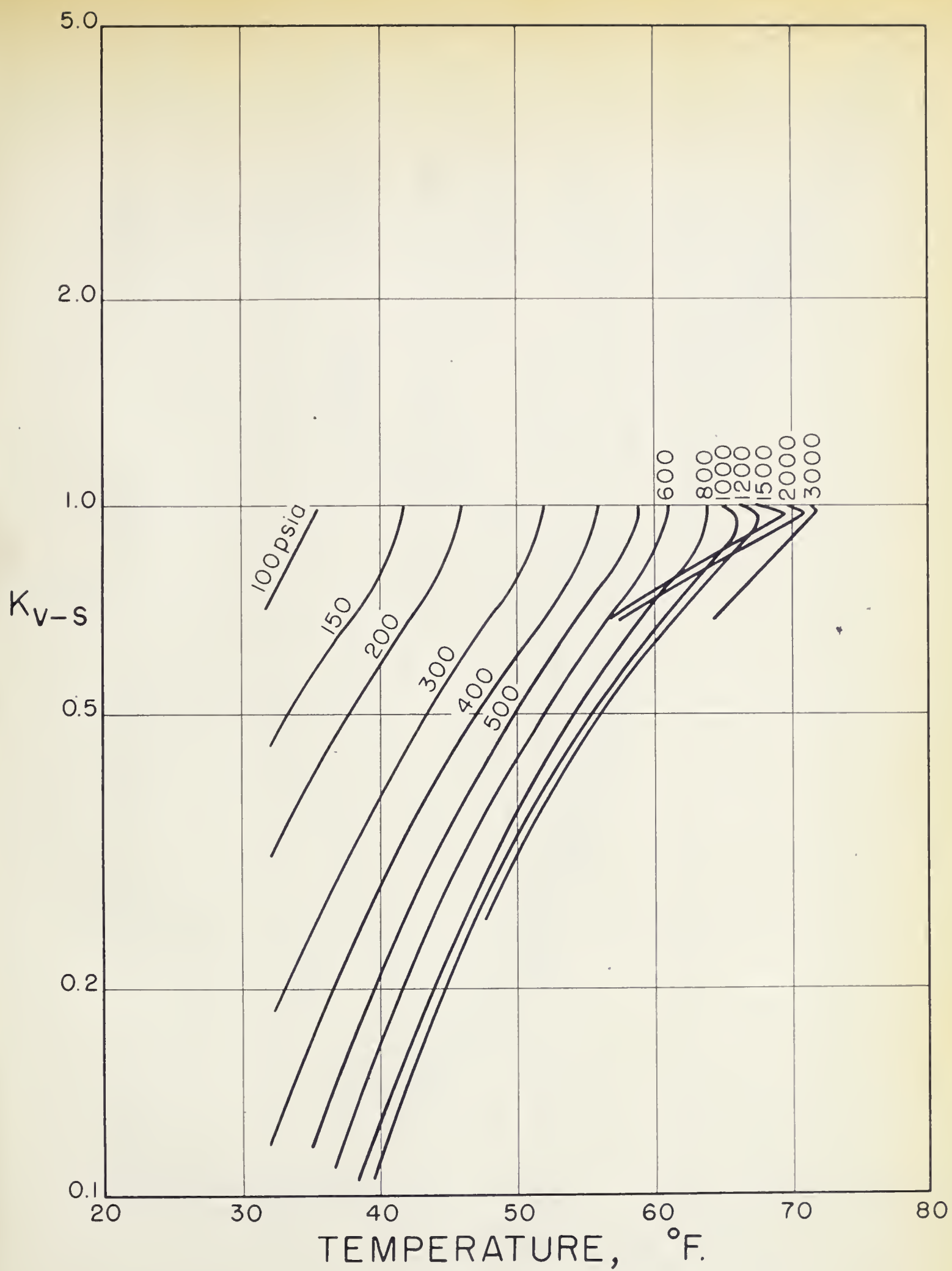


FIG. 4. SOLID-VAPOR EQUILIBRIUM RATIOS FOR ETHYLENE (6)



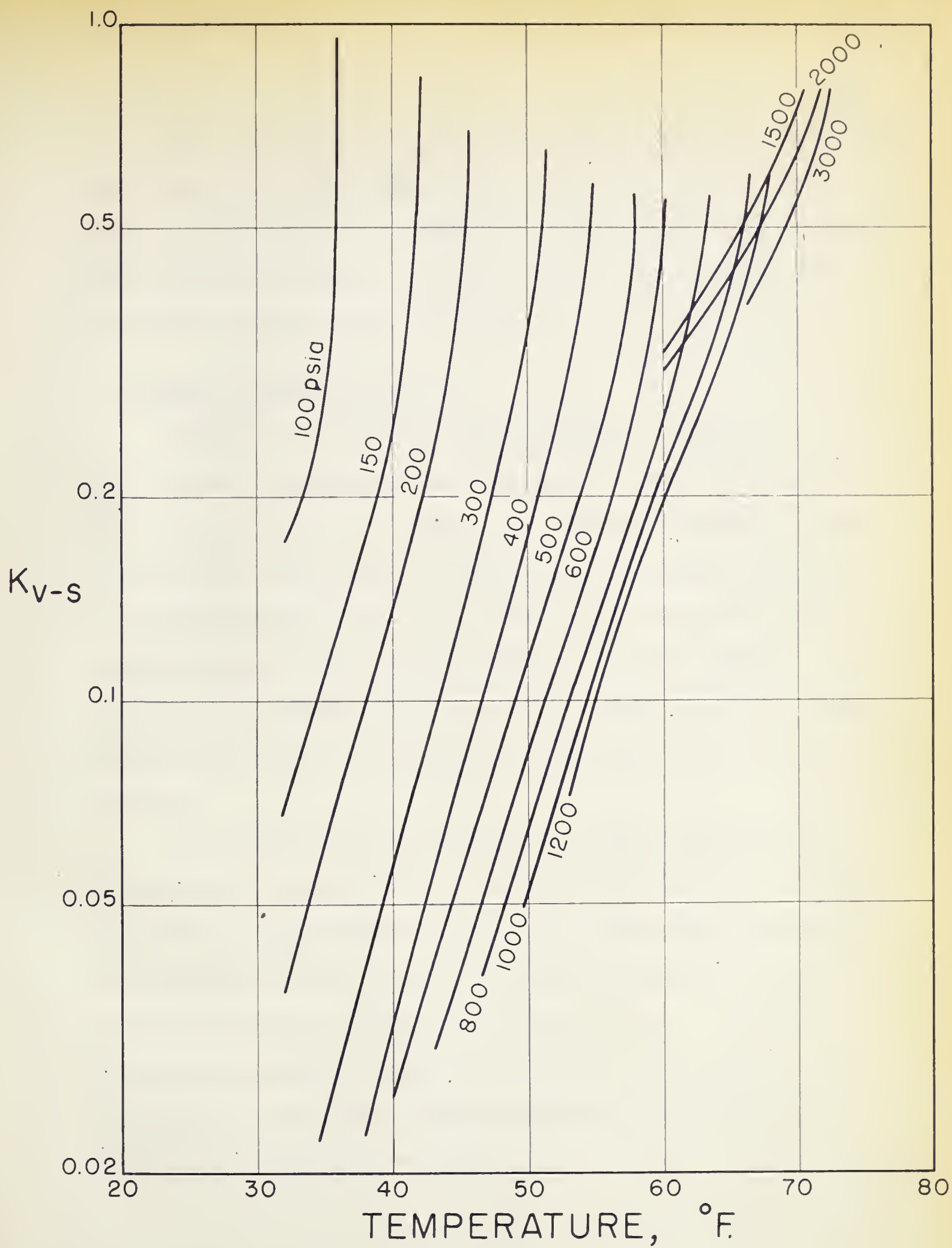


FIG. 5. SOLID-VAPOR EQUILIBRIUM RATIOS FOR PROPYLENE (6)



The assumptions and extrapolation used to prepare the equilibrium charts might leave considerable doubt as to their reliability but Carson and Katz found for a number of natural gases that the calculated hydrate forming pressure only differed about 10 percent from the experimental hydrate forming pressure.

(4) Crystal Structure of Hydrate

Although gas hydrates have been studied by a number of investigators, no definite crystal structure for these hydrates has been found until recently. Claussen (2) proposed a structure for the hydrate and it was subsequently varified using the x-ray technique of von Stackelberg and Muller (8). This x-ray investigation also yielded the result that there must exist two distinct hydrate structures corresponding to, (1) hydrates of small molecules or gases such as methane, and (2) hydrates of medium sized molecules such as ethylene.

The structure for the hydrate is a modified body centered cubic lattice. At each of the corners, and in the center of the cube, there is a pentagonal dodecahedral array of twenty water molecules. The dodecahedra at the corners of the cube are joined to adjacent corner dodecahedra by two additional water molecules. The body centered dodecahedron is attached to all of the eight corner dodecahedra through single hydrogen bonds and is also attached to twelve of the added water molecules.

Some data on the unit cubic cell are as follows:

Total number of water molecules	26
Number of small voids or holes	2
Number of medium sized holes	6

Hypothetical hydrating numbers

Filling all holes	$46/8 = 5.75 \text{ H}_2\text{O}$
Filling only medium holes	$46/6 = 7.67 \text{ H}_2\text{O}$

The hydrating hydrocarbon molecule fills in the void spaces in the lattice of water molecules. Agitation is generally necessary to allow the hydrocarbon molecule to fill this void space. However, if the two components are left together for a period of time, the hydrocarbon will move into the void space and hydrate will form.

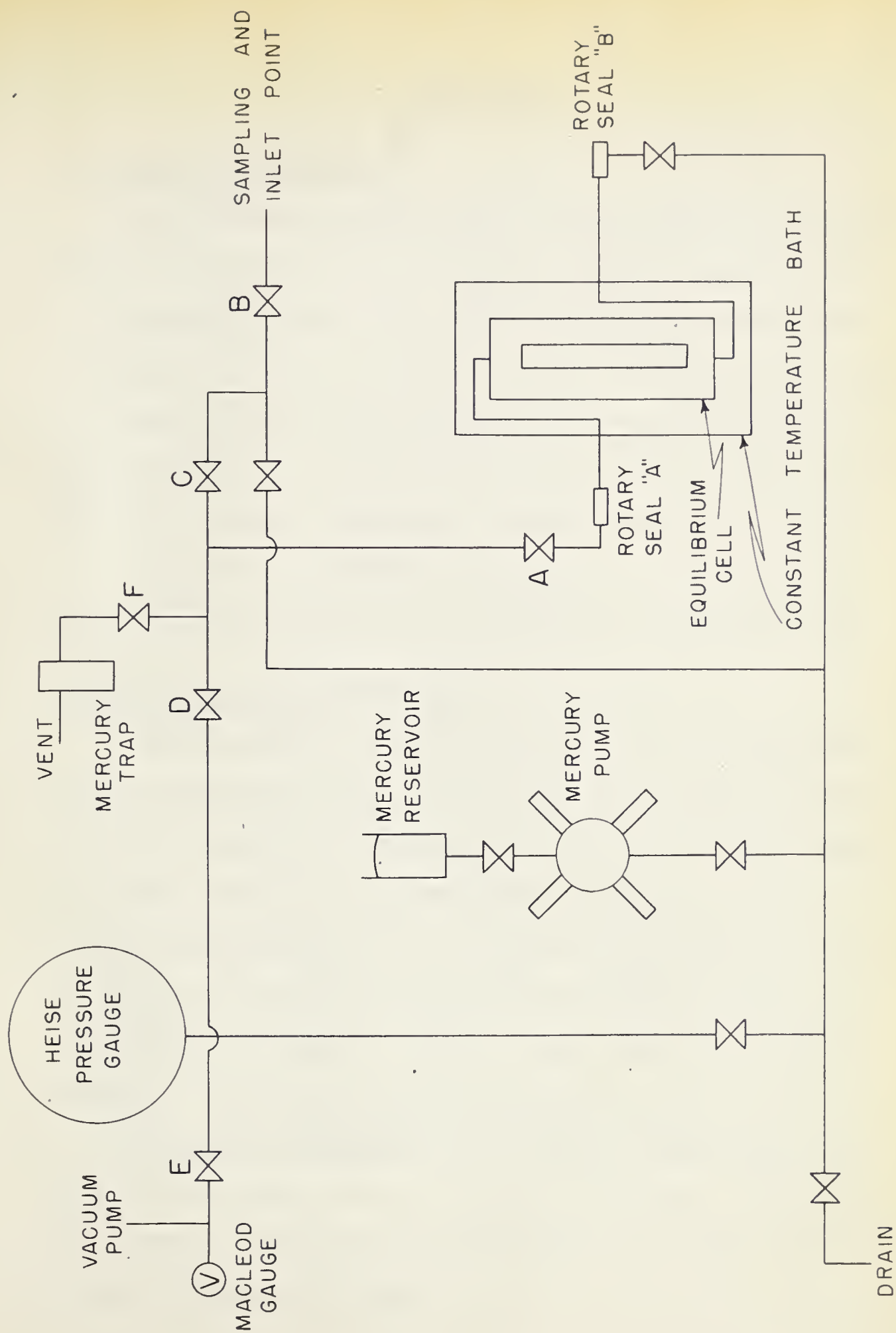


FIG. 6. SCHEMATIC APPARATUS ASSEMBLY



IV EXPERIMENTAL

(1) Experimental Apparatus

The apparatus assembly used in this experimental work was the same as that used by Otto for his work on hydrates and was similar to the apparatus used for other phase equilibrium studies at the University of Alberta. For the latter part of the experimental work, one change was made in the apparatus. This was the installation of a new equilibrium cell in place of the existing cell, so that study of the hydrate formation conditions at higher pressures was possible.

Figure 6 is a schematic diagram of the apparatus assembly after the installation of the new high pressure equilibrium cell.

(a) Low Pressure Equilibrium Cell

The low pressure equilibrium cell was the cell used by Otto for his studies on methane, ethylene and propylene water systems and mixtures of these gases with water. The cell was a Jerguson liquid level gauge capable of withstanding 2000 lb/in.²abs. at 100°F, with a volume of approximately 120 c.c. There was a sight glass on each side of the cell so that the contents inside were readily visible. The cell material was Type 304 stainless steel. The cell is shown in Figure 7.

This cell was enclosed in a 6 inch O.D. lucite cylinder so that the temperature of the cell could be controlled. The ends of the cylinder were fitted with lucite discs, and O-rings in order to prevent leaking of the coolant.

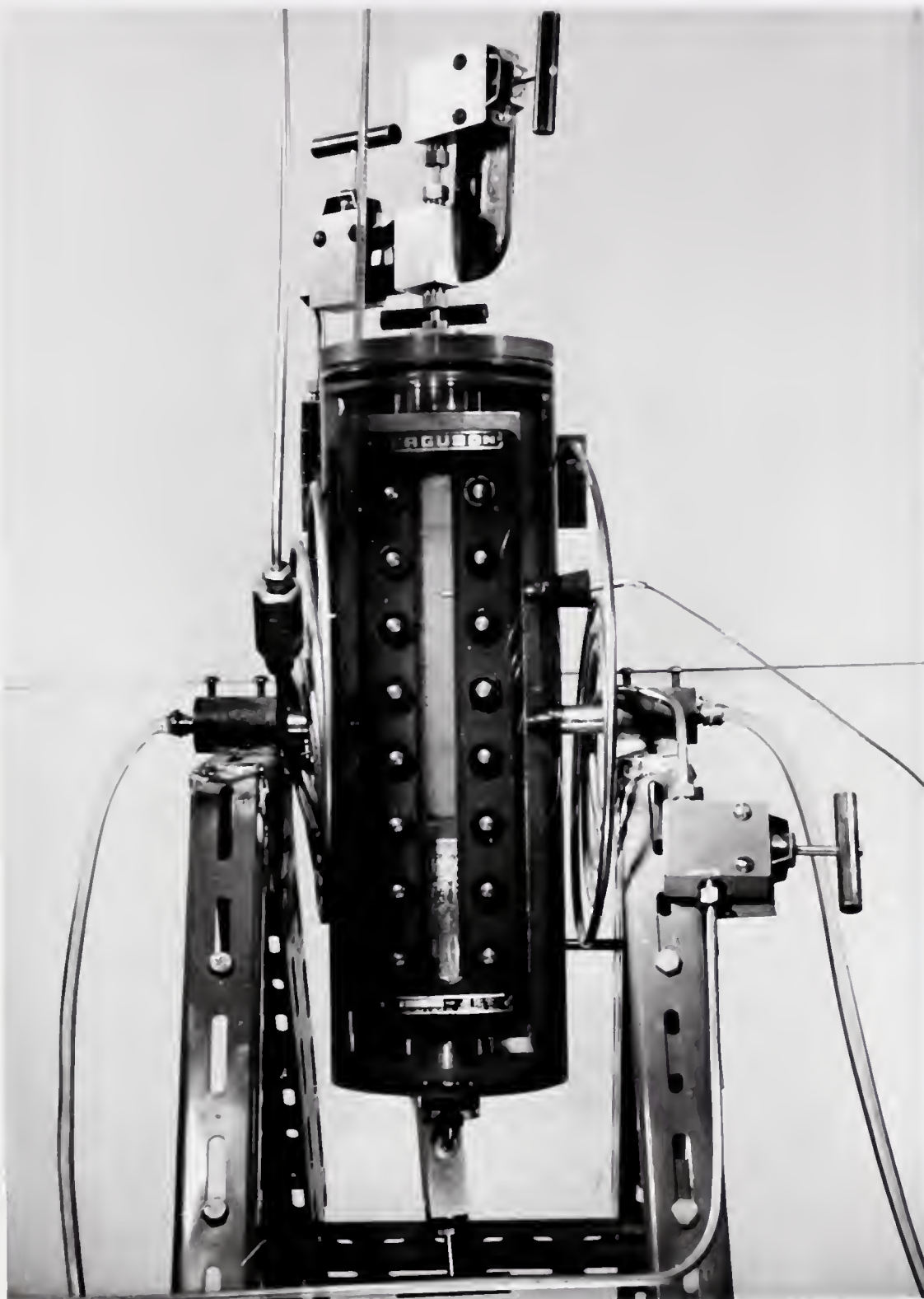


FIG. 7 LOW PRESSURE EQUILIBRIUM CELL

The equilibrium cell and lucite cylinder were mounted on two axial machined rods. These rods were coned at one end and fitted into holes countersunk in the equilibrium cell. The other end of the rod was fastened to a Dexion frame. This meant that the weight of the cell was transferred to the Dexion frame and no weight was on the lucite cylinder. The rods were hollow with a small hole in the end of the rod inside the lucite. This enabled the cooling fluid to be circulated in the cylinder. A light was placed behind the cell so that the contents inside were more readily visible. In order to allow rotation of the cell for agitation, there were two coils of Aminco tubing around the central axis of the cell.

(b) High Pressure Equilibrium Cell

The high pressure cell was a Penberthy liquid level gauge capable of withstanding 6000 lb/in.²abs. at 250°F, with a test pressure of 9000 lb/in.²abs. The cell was constructed of Type 316 stainless steel with sight glasses on both sides and had an approximate volume of 95 c.c. The cell is shown in Figure 8.

This cell was enclosed in an 8 inch O.D. lucite cylinder with lucite discs and O-rings on both ends to make the seal. A trunnion was used to allow the cell to rotate. The trunnion was fastened directly to the cell. This took the weight of the cell off the lucite. The cooling liquid was circulated through the trunnion into the lucite cylinder.

A crossectional view of the equilibrium cell is shown in Figure 9. The method of clamping and sealing the glass differs from conventional designs in that it relieves the glass of stress concentrations which

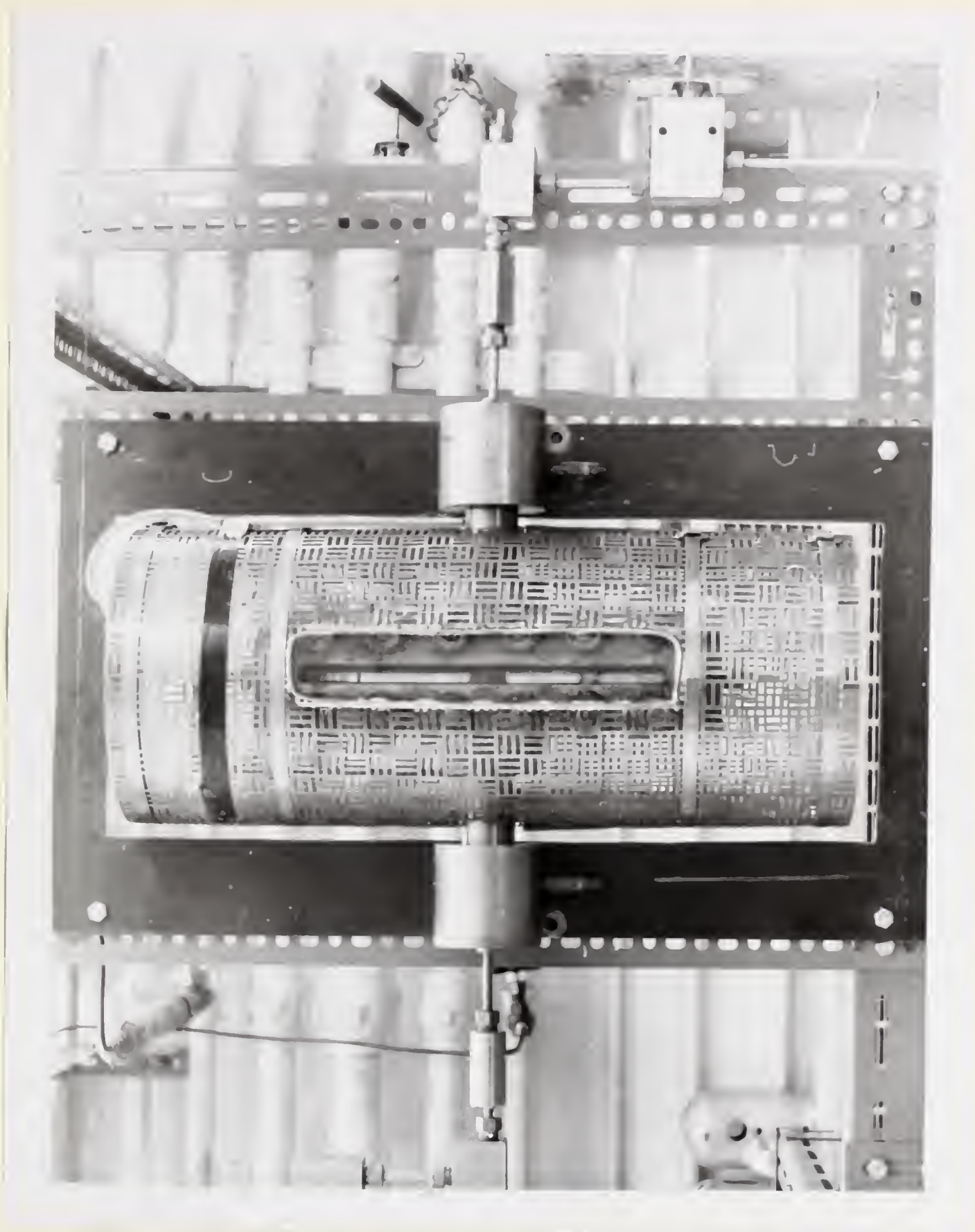


FIG. 8 HIGH PRESSURE EQUILIBRIUM CELL

are inevitable when the load necessary to effect the seal depends upon the pressure applied by the bolts. In this design, the glass becomes a floating member between two solidly bolted blocks of rigid steel and therefore is not subjected to such strains as produced by eccentric bolt loading and uneven bolt tension. This design will work providing there are gasket retainers present to prevent the gasket from extruding between the glass and the steel, and thus breaking the seal. When the cell was assembled these gasket retainers were damaged and could not be used. It was found that without the retainers, pressures exceeding about 100 lb/in.²abs. could not be achieved. Several means were tried to make a better seal, such as increasing the cushion size to make the glass fit closer to the liquid chamber. This was not successful, however. Up until this point, neoprene gaskets were being used. These gaskets act the same way as an O-ring does to make the seal. It was decided to use teflon as the gasket material in order to stop the tearing and extruding action. This was found to be highly successful. There was a distinct disadvantage in using teflon, however. In order to make a seal with the teflon gaskets, a larger strain was put on the glass in compressing the more rigid gasket material. For this reason pressures in excess of 5000 lb/in.²abs. were not attempted.

To enable the low pressure cell to rotate, coils of Aminco tubing were placed around the central axis of the cell. These coils were done away with when the high pressure equilibrium cell was installed. In their place, rotary seals shown in Figure 6 were used.

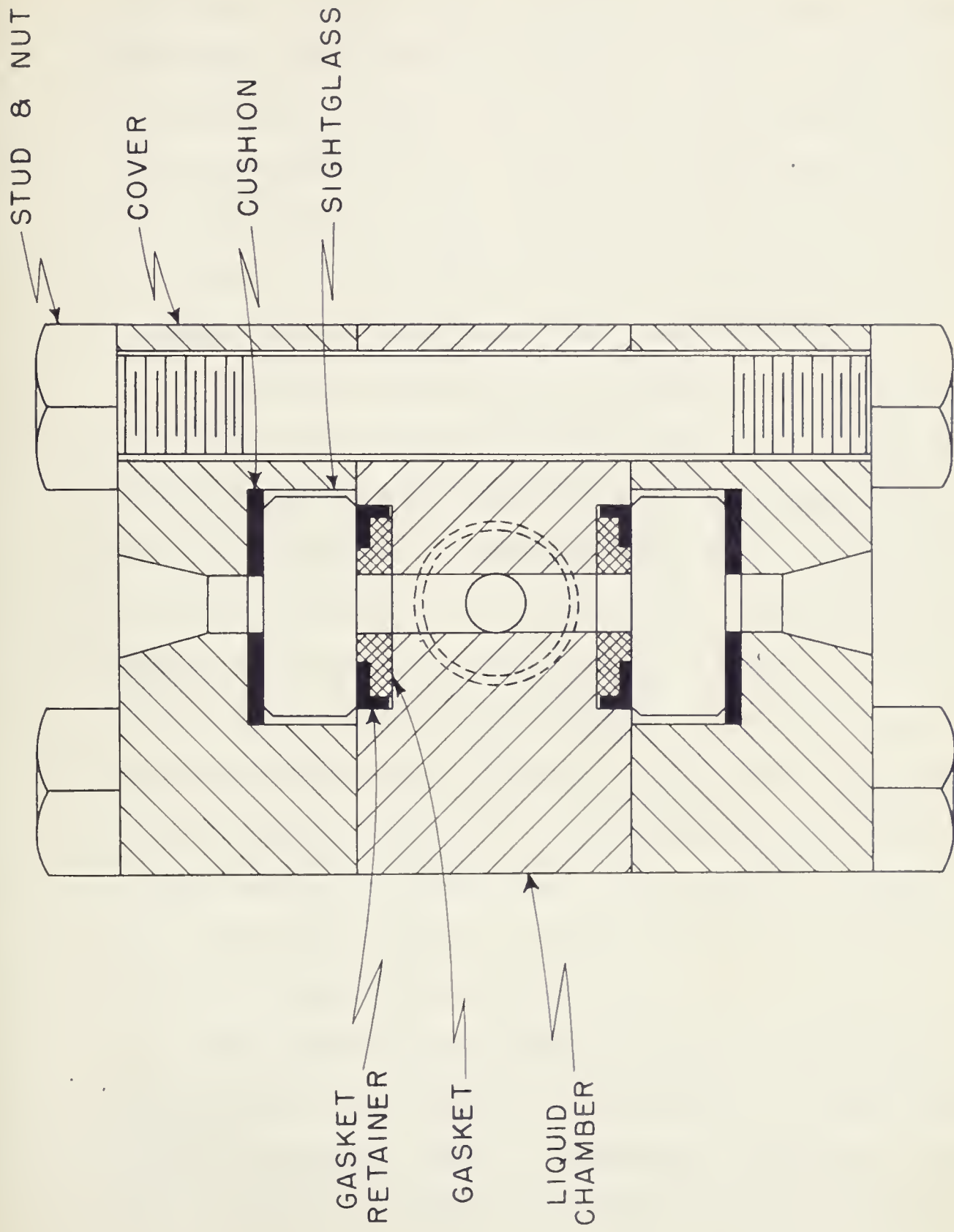


FIG. 9. CROSSECTIONAL VIEW OF PENBERTHY
LIQUID LEVEL GAUGE

(c) Rotary Seals

These rotary seals were found to be quite adequate and more convenient than the coils of tubing previously used. Two types of seals were used. They are shown in Figures 10 and 11. Figure 10 shows the first type of seal made. Two of these were made and were identical except one employed four O-rings and the other three O-rings. Also in the three O-ring seal, the machined tolerances were not as close as in the other. The seal with the three O-rings eventually failed in use and was replaced by the type of seal shown in Figure 11.

The moving cylinder of the seal shown in Figure 10 was made of 1 inch O.D. Type 316 stainless steel. One end was drilled and threaded for the ordinary Aminco connection to the equilibrium cell, and the other to accommodate the stationary axle. This axle was machined out of 316 stainless steel with a 3/32 inch I.D. Two thrust plates with a bearing cage between were used to enable the axle to be tightened down and still allow the cylinder to rotate. The O-rings made the final seal. As previously mentioned, the seal with the three O-rings failed. The first O-ring was pushed out of its groove and extruded between the cylinder and the stationary axle. The O-rings were replaced but the same thing occurred again. For this reason the new seal shown diagrammatically in Figure 11 was made.

This seal was made out of a 304 stainless steel Aminco tee. Two parts of the tee were drilled out approximately 1/2 inch, and to the width of the original thread. This block is stationary. The rotating axle was made out of Aminco high pressure tubing and one end was welded

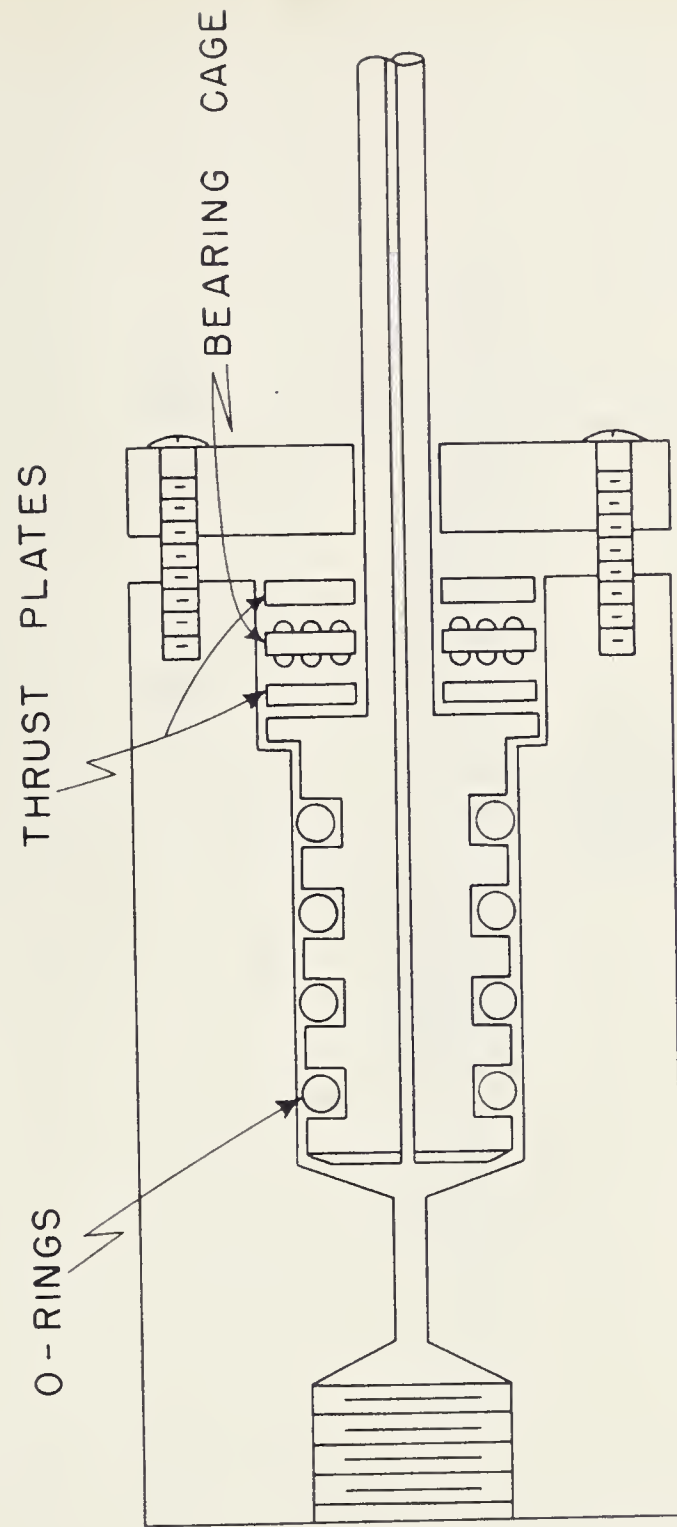


FIG. 10. ROTARY SEAL "A"

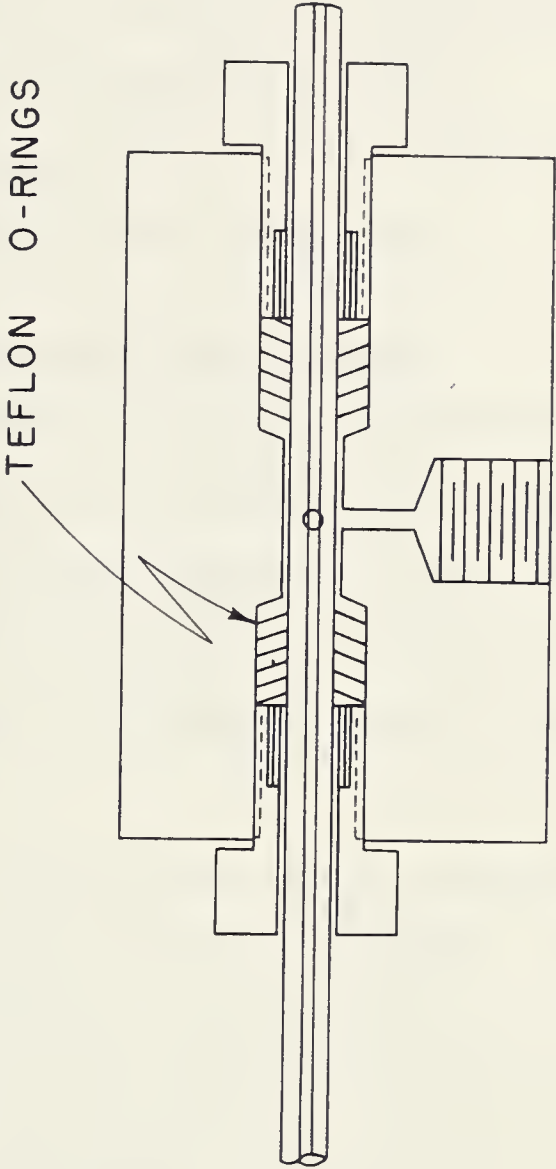


FIG. II. ROTARY SEAL "B"

shut. A 1/16 inch hole was drilled through the side into the inside of the tubing. There was enough clearance between the tubing and the block so that mercury was around the tubing and the pressure therefore transmitted to the cell at all times. Teflon O-rings were tightened down by steel sleeves enclosed in Aminco nuts to make the seal. This rotary seal was found to be very effective and no leaks of any kind were encountered during the remainder of the tests.

The 316 stainless steel was used to enable the study of H_2S or other corrosive gases in future experiments.

(d) Control and Measurement of Temperatures

The temperature of the equilibrium cell was controlled by circulating a coolant from an auxiliary bath through the lucite cylinder jacketing the equilibrium cell. Varsol was used as the bath fluid when using the low pressure cell and Bayol D, which had a higher flash point, was used for the coolant around the high pressure equilibrium cell.

The auxiliary bath was made out of a cork-insulated tank equipped with an immersion pump to circulate the liquid. Cooling of the fluid was accomplished with a Freon refrigerating unit, the coils of which were immersed in the auxiliary bath. Two 500 watt immersion heaters were used for heating purposes. One of these heaters was connected to a 500 watt variac. The temperature in the bath was controlled by an American Instrument Co. bi-metallic strip controller. This controller was connected through a relay and transformer to the refrigerator. No control was used on the heating of the bath. This method of control

was satisfactory and kept the temperature of the bath constant within $\pm 0.5^{\circ}\text{F}$.

The temperature inside the cell was measured by an iron-constantan thermocouple inserted through the side of the cell. This thermocouple was made out of Aminco high pressure tubing. The calibration curve for this is shown in Figure 19. A thermometer was also immersed in the bath to give an indication of the temperature.

(e) Pressure Measurement

The pressure in the cell was adjusted by injecting or withdrawing mercury with a Ruska Instrument Corporation positive displacement pump. This pump had an approximate volume of 100 c.c. and was rated at 8000 lb/in.² abs.

A Heise Bourdon tube pressure gauge with a range 0 - 5000 lb/in.² abs. was used for pressure measurement. This gauge was calibrated with a dead weight tester. Corrections to the indicated pressure in the cell were made for atmospheric pressure and for the head of mercury between the gauge and the cell.

(f) Apparatus - General

All tubing and valves used were superpressure equipment made by the American Instrument Company, Inc. The tubing used was 1/4 inch O.D. and 3/32 inch I.D. made of 304 stainless steel and rated at 30,000 lb/in.² abs. at 100°F. All valves were made of 304 stainless steel and rated at 30,000 lb/in.² abs. The equilibrium cell and all the tubing and valves were mounted on a framework of Dexion.

A General Electric duo seal vacuum pump was used to evacuate the system to a pressure of 0.02 mm. of mercury. The vacuum obtained was measured with a MacLeod Gauge.

A Jerguson liquid level gauge rated at 3000 lb/in.²abs. at 100°F was used to transfer gas into the equilibrium cell. This cell could not be used for experimental work since it had only one sight glass and the contents of the cell would not be visible.

It was found that after a few hydrate formation points were found, the mercury would become dirty and the glass windows of the cell would become coated. When this started to occur the mercury was cleaned in a Mercury Oxifier made by the Bethlehem Apparatus Co. A mercury filter, type F (Gold Adhesion principle) was used to filter the oxified mercury. This was also supplied by the Bethlehem Apparatus Co.

(g) Purity of Hydrocarbons Used

The methane used in this work was supplied by Phillips Petroleum Company and had a purity of 99.8 mole percent. The ethylene was obtained from the Matheson Company, Inc., and was "C.P. grade," having a minimum purity of 99.5 mole percent. The propylene was obtained from Phillips Petroleum Company and had a minimum purity of 99 mole percent. Chromatographic analysis of these gases showed that these specifications were met. No further purification of the gases was attempted.

(2) Experimental Technique

(a) Introducing Components Into Cell

All the gas and liquid was expelled from the cell by filling the

cell and the tubing up to valve A (Fig. 6) with mercury. With valves C, D and E open and valve A closed, the system was evacuated. E, D and C valves were closed and the line from valve F to valve A was filled with water. Valves A, B and C were opened and gas forced the water into the cell. The cell was then pressured. When a two component gas was used in the equilibrium cell, the gas from the lower pressure tank was introduced first.

Some difficulty was encountered in introducing the water into the cell in this manner. When the hydrocarbon gas was expanded across valve B to force the liquid water into the cell, cooling of the gas resulted. This cooling was significant enough to lower the temperature of the gas to the hydrate forming region and hydrates formed. These hydrates blocked valves and tubing and no gas could be added to the cell until the temperature had risen enough for the hydrates to melt. This took as long as one hour in some cases.

(b) Forming of Hydrate

After the aqueous liquid and the gas had been introduced into the equilibrium cell, the pressure in the cell was raised by injecting mercury into the cell from the mercury pump. The contents of the cell were agitated to ensure that the gases were thoroughly mixed. The temperature of the cell was then lowered to 5 to 10°F below the formation temperature of the hydrate. More agitation of the cell caused the hydrate to form.

For two component equilibria (one gas + water) in three phases, L_1HV , there is one degree of freedom, so the melting point of the

hydrate is the same as the formation point. To obtain the initial formation point for the two component equilibria, the hydrate was formed and the temperature was raised slowly until the hydrate just started to melt. The pressure and temperature were then recorded.

For three component equilibria (two component gas + water) in three phases, there are two degrees of freedom and the hydrate will melt over a range of temperatures at a given pressure. To determine the incipient hydrate formation for three component equilibria, the hydrate was formed and the temperature raised very slowly until the hydrate just started to melt. This point could also be detected by an increase in pressure. The hydrate was melted until only a very few small crystals were left. The temperature was then lowered a few tenths of a degree and crystals of hydrate would form on the glass window of the cell. The temperature was again raised very slowly and the pressure and temperature recorded where these crystals started to melt.

(c) Sampling

For the three component equilibria where the hydrocarbons were above the critical conditions, one vapor sample was obtained at the beginning and one at the end of a series of equilibrium points. The samples were collected in evacuated glass bombs and analysed by gas phase chromatography. The two vapor samples taken for a given total composition in the cell checked very well.

For the three component equilibria where the hydrocarbon was below the critical conditions, vapor samples were taken at every

equilibrium point. The system, methane-propylene-water, was of this type. This sample was removed under isobaric and isothermal conditions by increasing the level of the mercury in the cell as gas was removed. It was found that for any fixed total composition under investigation, the vapor composition stayed constant. This means that there was no liquid propylene present. The samples were collected in evacuated glass bombs and analysed on the Kromo-Tog.

In the determination of experimental K values, both the hydrate and vapor composition in equilibrium were required. After the hydrate was formed, a vapor sample was taken under isobaric and isothermal conditions. The remaining vapor and liquid was removed from the cell by increasing the level of the mercury in the cell as gas was removed, again under isobaric and isothermal conditions. A stainless steel screen in the top of the equilibrium cell retained the hydrate. After all of the phases but the hydrate were removed, the level of the mercury was lowered and the hydrate melted. A gas sample was then taken and analysed.

(d) Chromatographic Analysis

All vapor analyses were done by gas-liquid partition chromatography. A type K-2 Kromo-Tog supplied by the Burrell Corporation was used, employing a packed column of tri-isobutylene liquid supported on firebrick. Calibration curves of peak height versus mole percent were prepared for methane, ethylene and propylene. These curves are shown on Figure 20 in the Appendix and the data presented in Table X in the Appendix.

To calibrate the Kromo-Tog, a measured amount of gas from a gas burette was collected in an evacuated glass bomb. In this way different mixtures of the three gases, methane, ethylene and propylene, could be made up. The samples were then passed through the Kromo-Tog, and assuming volume percent is equal to mole percent, curves of peak height obtained versus mole percent were made.

A significant amount of difficulty was encountered in obtaining a consistent calibration for the Kromo-Tog. The first column used was an Apiezon M grease supported on firebrick. With this column a complete separation of methane and ethylene was not possible. This is because the retention time of the methane and ethylene in the column was nearly the same. This means that the peaks for ethylene and methane will overlap and thus the amount of one component in the mixture will influence the peak height of the other. Both the temperature of the column and the helium carrier gas rate were reduced in order to spread the methane and ethylene peaks out. This did not prevent the overlapping of peaks however. A new column was tried using tri-isobutylene supported on firebrick as the packing material. This gave a very good separation. The column was operated at room temperature and the helium carrier gas flow rate was 40 ml/min.

It was found that changes in the room temperature affected the peak height obtained to a considerable extent. Changes in flow rate had little effect on the peak height. This meant that the composition obtained from the peak height changed as the room temperature varied. It was found from the literature that this can be corrected for by

increasing or decreasing the percentage of each component in the mixture in proportion to the percentages obtained from the calibration curve so that the total percent was 100. The same gas mixture was analysed on the Kromo-Tog at various temperatures and it was found that after the corrections, the percentages were the same.

Chromatographic analysis proved to be a very fast and accurate method for determining the percentage of known constituents in the sample.

V EXPERIMENTAL RESULTS

(1) Three Phase Equilibria for Two Component Systems(a) Methane-Water System

The hydrate formation conditions for this system have been determined by a number of investigators. The purpose of obtaining this equilibrium data was to check the pressures and temperatures at which hydrate starts to form.

The pressures and temperatures where hydrate starts to form for the water-rich liquid, hydrate and vapor equilibria were determined between 1257 lb/in.²abs. and 52.7°F and 4992 lb/in.²abs. and 72.7°F. These data are recorded in Table V, in the Appendix and are plotted on Figure 13 along with data obtained by Otto (6). Otto's data were extended from 991 lb/in.²abs. and 48.5°F to 4992 lb/in.²abs. and 72.7°F. These data were consistent with the data obtained from Otto.

(b) Ethylene-Water System

The hydrate forming conditions for the three phase equilibria L₁HV were extended from 1963 lb/in.²abs. and 68.3°F to 4954 lb/in.²abs. and 75.8°F. These data are shown in Table VI in the Appendix and pressures and temperatures for hydrate formation are plotted on Figure 12. Published data by Diepen and Scheffer and data obtained by Otto are plotted on Figure 12. Diepen and Scheffer presented data up to 793 lb/in.²abs. and 64.4°F and Otto extended this data to 1963 lb/in.²abs. and 68.3°F. In this work the data covers a range from 2137 lb/in.²abs. and 68.8°F to 4954 lb/in.²abs. and 75.8°F. The

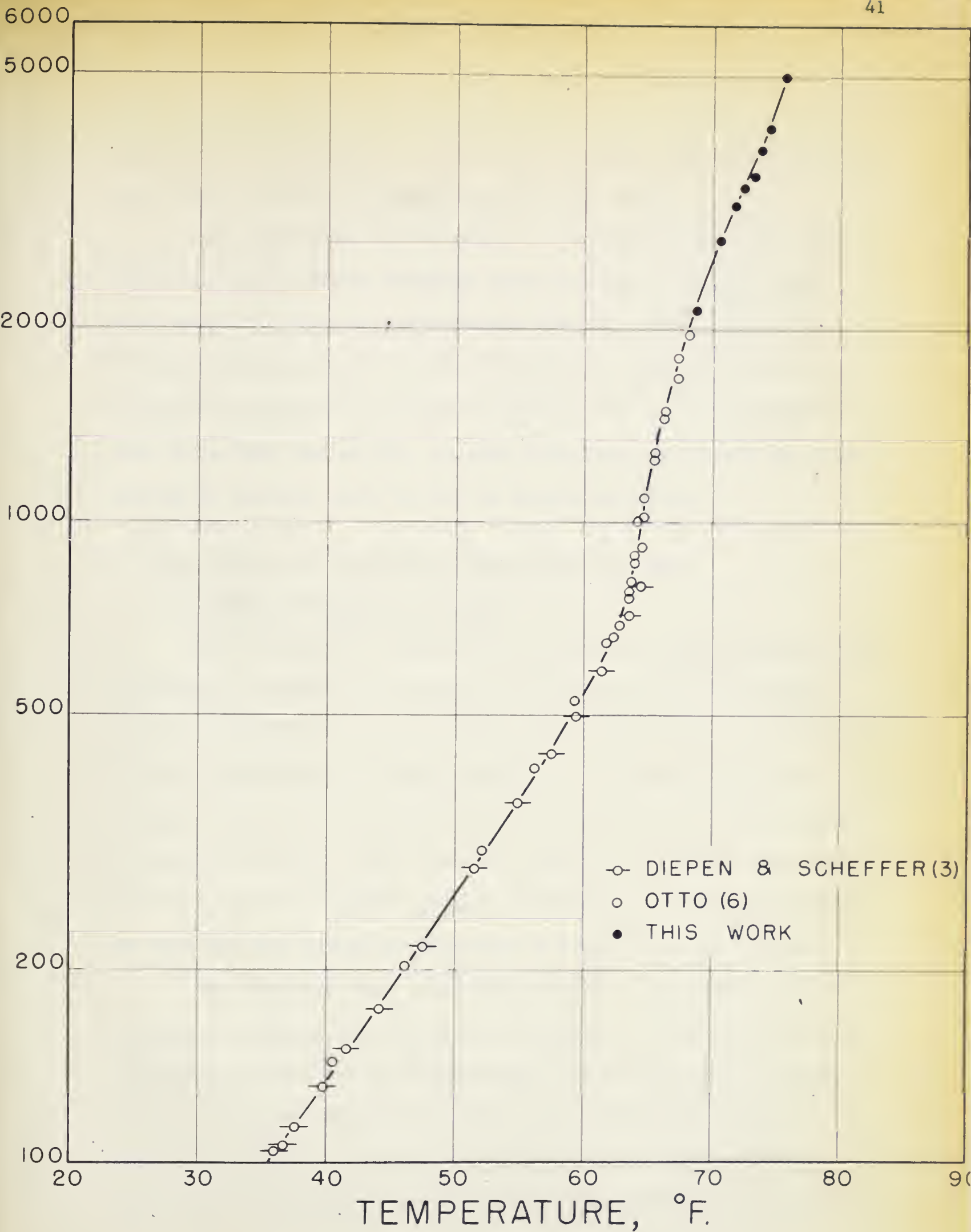


FIG. 12. CONDITIONS FOR HYDRATE FORMATION IN ETHYLENE-WATER SYSTEM



experimental data obtained in this work was found to be consistent with Otto's data and was a smooth extension of his curve.

Otto found that approximately at 700 lb/in.²abs. and 62.9°F the slope of the hydrate formation curve rose quite sharply. This slope decreases again at approximately 1100 lb/in.²abs. and 64.9°F. In this work the slope of the curve was found to decrease more as the pressure was increased and became relatively constant at approximately 2500 lb/in.²abs. and 69.7°F. At 3500 lb/in.²abs. and 73.0°F the slope started to increase again but not as sharply as before.

(2) Three Phase Equilibria for Three Component Systems

(a) Methane-Ethylene-Water System

The pressures and temperatures for which hydrate begins to form in mixtures of methane and ethylene for the three phase equilibria, L₁HV has been extended to approximately 5000 lb/in.²abs. Otto presented data for the system up to 2000 lb/in.²abs. These data are shown on Figures 13 and 14 along with the data Otto obtained. On these figures are plotted the three phase equilibria, water-rich liquid, hydrate and vapor for the two component systems of methane-water and ethylene-water. The data for this system are presented in Table VII in the Appendix.

For pressures below about 600 lb/in.²abs. the curves for the mixtures of ethylene and methane have approximately the same slope and parallel the curves for the methane-water and ethylene-water systems. For the low concentrations of ethylene, the curves approximately parallel the curve for the methane-water system up to about 5000 lb/in.²abs., the highest pressure where data were taken in this work.

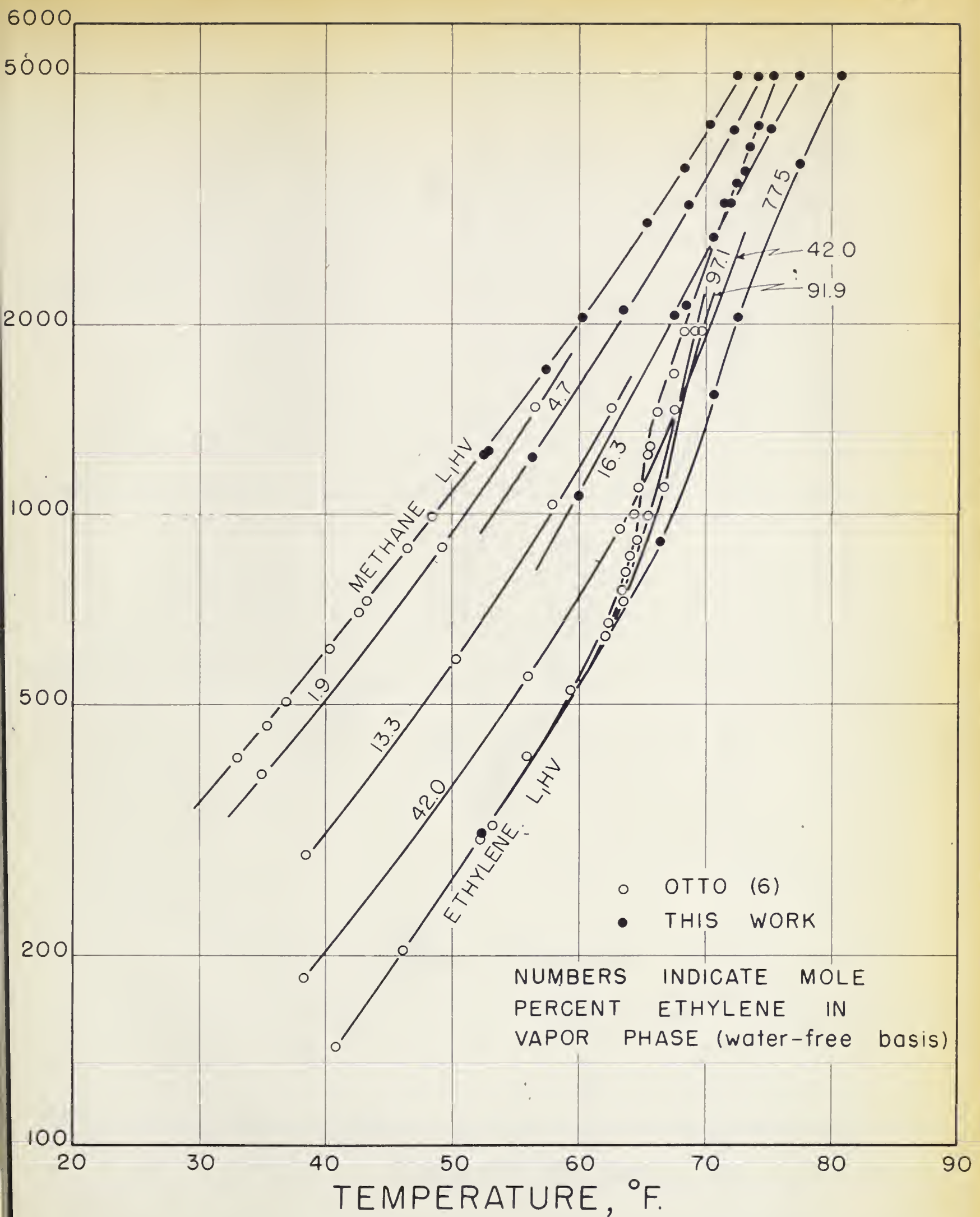


FIG. 13. CONDITIONS FOR HYDRATE FORMATION IN METHANE-ETHYLENE-WATER SYSTEM



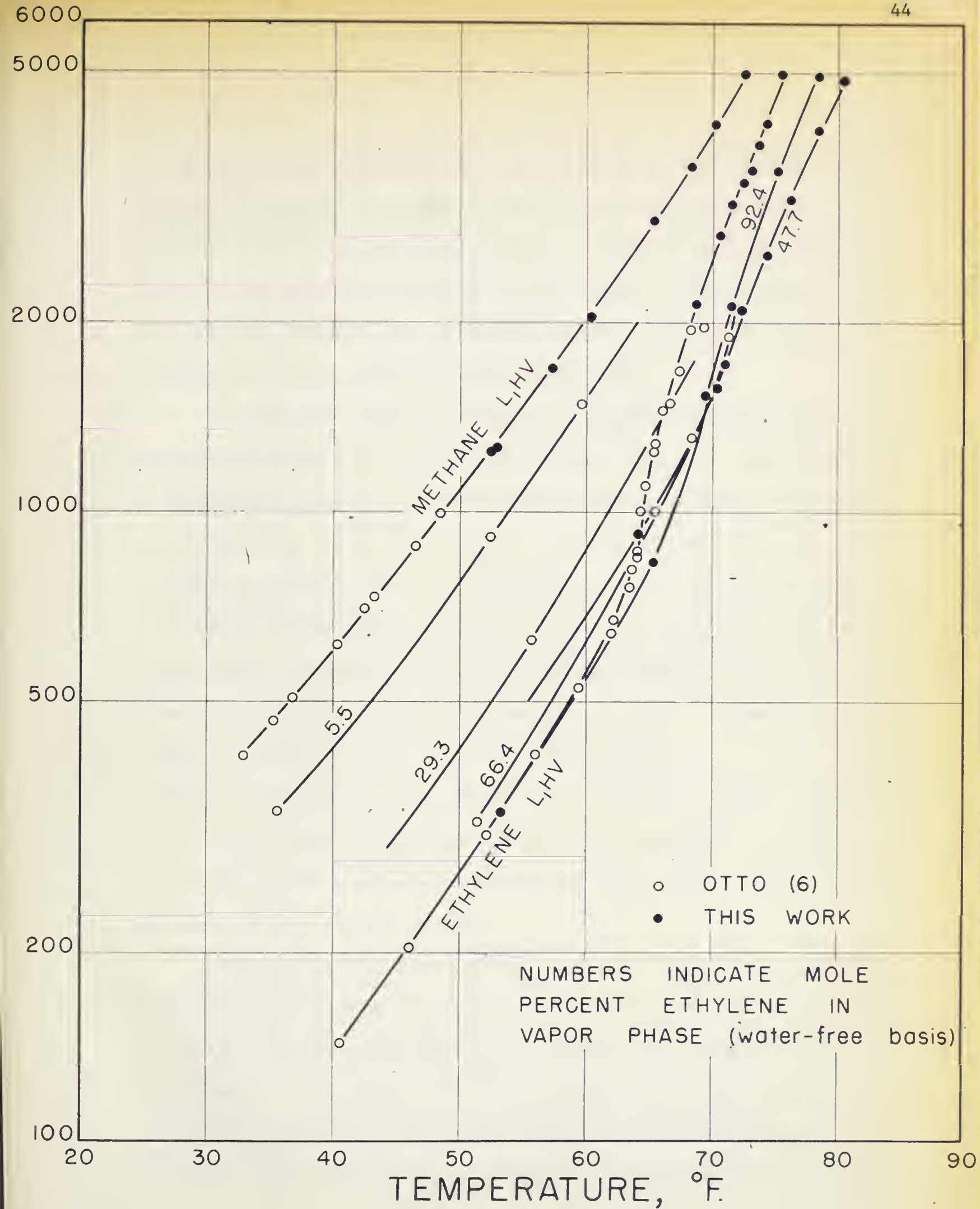


FIG. 14. CONDITIONS FOR HYDRATE FORMATION IN METHANE-ETHYLENE-WATER SYSTEM

It was also found that below about 450 lb/in.²abs., for ethylene compositions greater than about 70 mole percent, the three phase equilibria curves for the methane-ethylene-water system fell on the curve for the ethylene-water system. Above about 600 lb/in.²abs. the slopes of the curves began to increase and this increase became more pronounced for the higher ethylene concentrations.

It was found that the curves for the methane-ethylene-water system crossed the curve for the ethylene-water system. This occurs at an ethylene composition of about 10 mole percent. This crossing is due to the sharp increase in slope of the ethylene-water curve as described previously. For the higher concentrations of ethylene the slope of the curves first increased and then decreased again, similar to the curve for ethylene-water. For ethylene compositions of about 90 mole percent and greater, the slope of the curves increased very sharply at about 900 lb/in.²abs. and crossed the curves for lower ethylene concentrations. This means that the hydrate forming temperature at a given pressure for the high ethylene composition is higher than the temperature for ethylene-water but lower than the temperature for say a 70 mole percent mixture.

This can be seen more clearly in Figure 15 which is a crossplot drawn from Figures 13 and 14. It is a plot of hydrate forming temperature versus mole percent ethylene in the vapor phase with pressure as the parameter. From this plot it can be seen that at high pressures a maximum hydrate forming temperature occurs for the methane-ethylene mixtures. This is higher than the hydrate forming temperature for either

the methane-water or ethylene-water systems. At 5000 lb/in.²abs. the maximum formation temperature is approximately 81.4°F at an ethylene vapor composition of about 63 mole percent. Below about 500 lb/in.²abs., the ethylene-water system has the maximum hydrate formation temperature, but for pressures in excess of this the methane-ethylene mixture will have the highest formation temperature.

It is conceivable that for pressures in excess of 5000 lb/in.²abs., the curve for ethylene-water will cross the curve for methane-water and thus will have a lower incipient hydrate formation temperature.

(3) Experimental K Values

Otto (6) determined the three phase equilibria, water-rich liquid, hydrate and vapor for one gas mixture of methane, ethylene and propylene. He then calculated the theoretical hydrate forming curve for a gas of this composition. He found that there was an error in this prediction of approximately 25 percent. For this reason an attempt was made to obtain experimental K values by analysing both the vapor and the hydrate.

The first system used was methane-ethylene-water. After the hydrate was formed a vapor sample was taken. The liquid and vapor contents of the cell were removed and a vapor sample of the melted hydrate was taken. Then, using the analysis of the vapor above the hydrate and the hydrate analysis, the solid-vapor equilibrium ratios were calculated. It was found, however, that no consistent results could be obtained. This is because the vapor composition is constantly

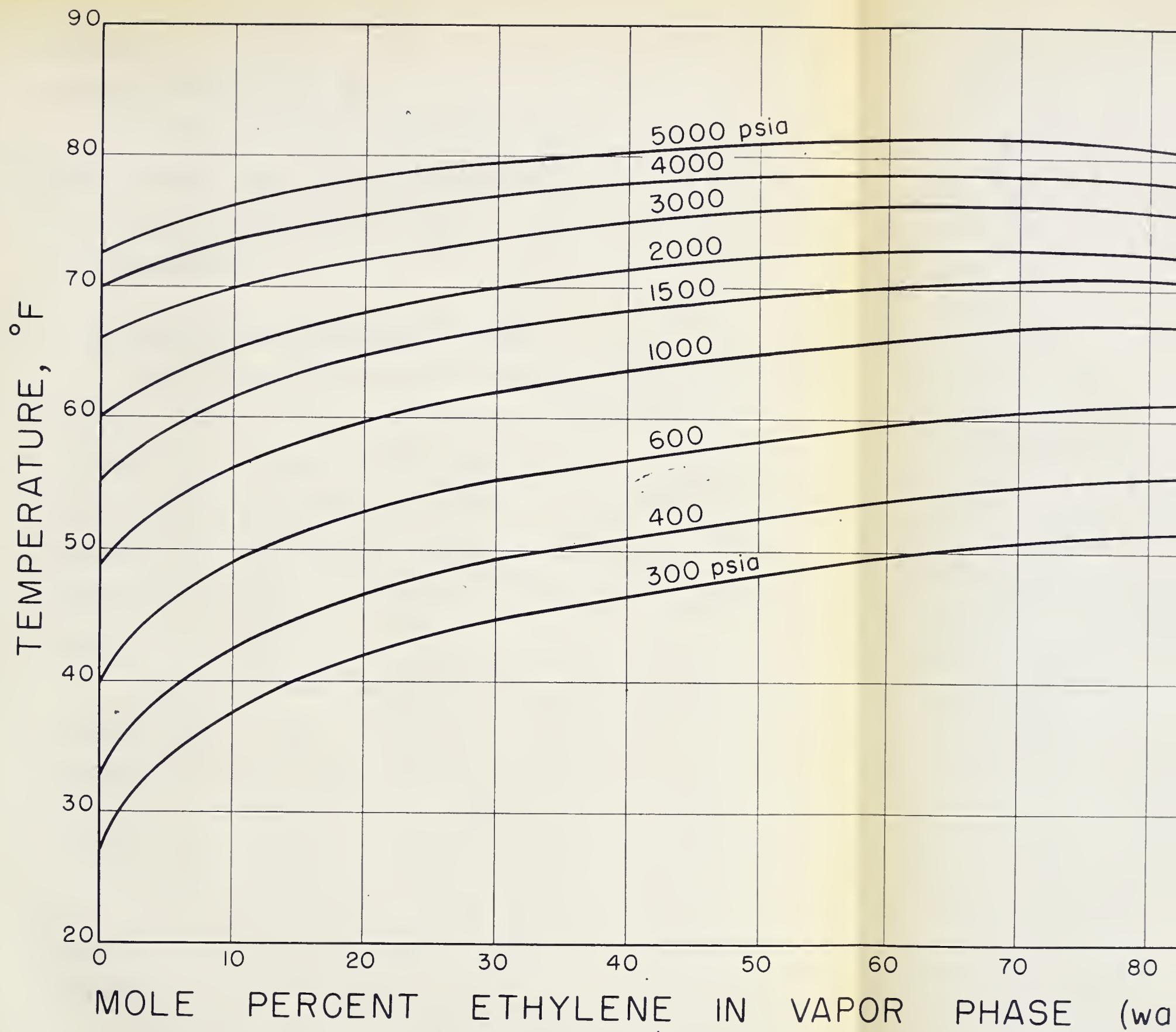
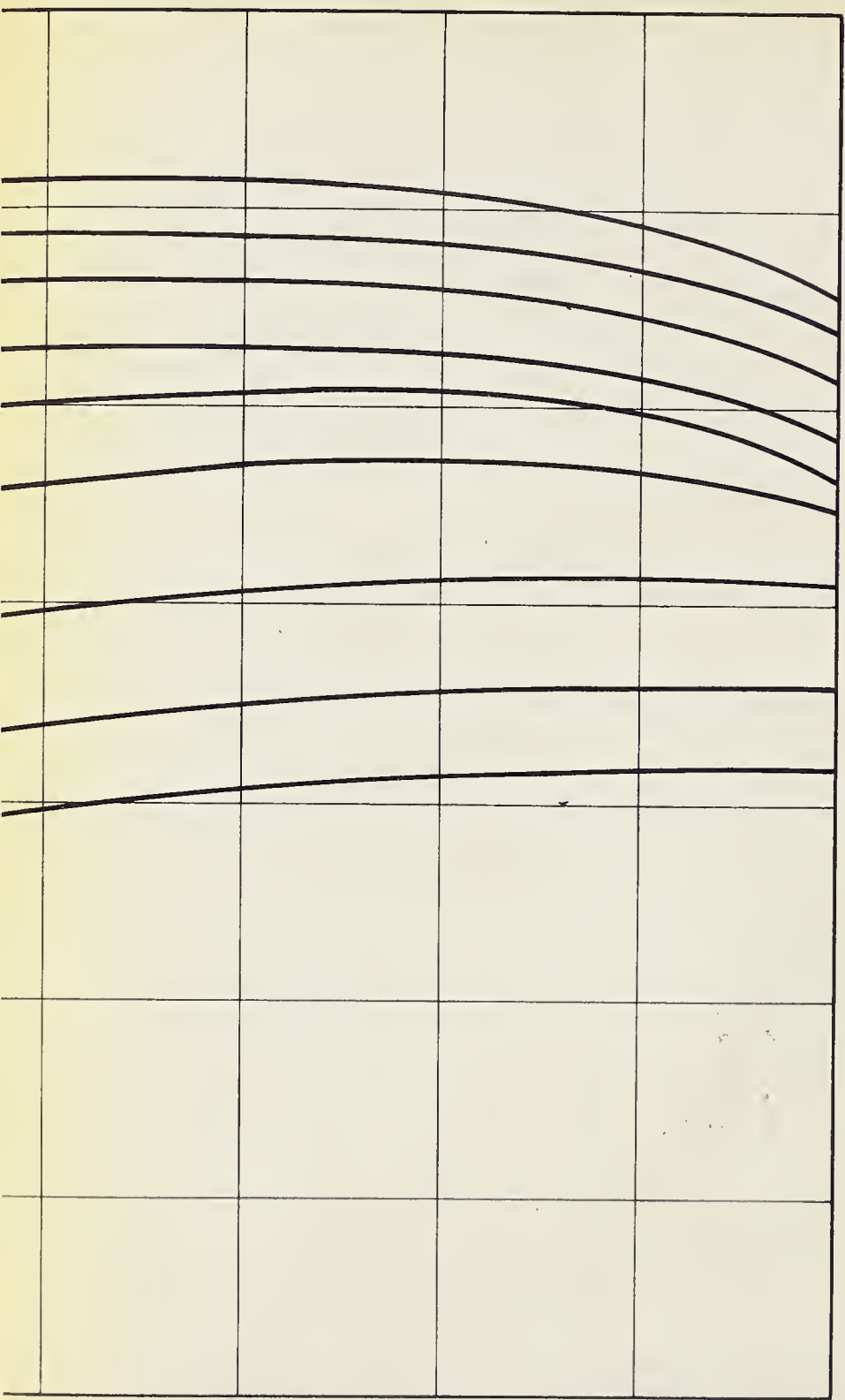


FIG. 15 HYDRATE FORMING CONDITIONS FOR METHAN MIXTURES



OR PHASE (water-free basis)
S FOR METHANE - ETHYLENE

changing with time and the K value will then depend on how long the hydrate is allowed to form.

The system, methane-propylene-water, was tried next. With the liquid propylene present, the vapor composition would stay constant. Several runs were made with this system but again no consistent results could be achieved.

(4) Methane-Ethylene-Propylene-Water Systems

The incipient hydrate formation conditions for the three phase equilibria L₁HV for various compositions of methane, ethylene and propylene in equilibrium with water-rich liquid were determined. These curves are plotted on Figures 16, 17 and 18, along with the predicted conditions for hydrate formation. The data of Otto, along with his predictions, are plotted on Figure 16. The data are presented in Table VIII in the Appendix.

The calculated hydrate conditions are determined by using the relationship $\sum \frac{y}{K} = 1$ where y is the mole fraction of the component in the vapor phase and K is the solid-vapor equilibrium ratio for the component at the pressure and temperature of hydrate formation. To use this equation, a temperature is assumed at a given pressure and the K value taken from Katz's curves for methane and Otto's curves for ethylene and propylene. Temperatures are assumed until the above relationship is equal to unity.

The hydrate forming conditions for three mixtures of methane, ethylene and propylene were determined. The approximate deviation in the temperature was from 1.7 to 3.9 percent at a given pressure. For a

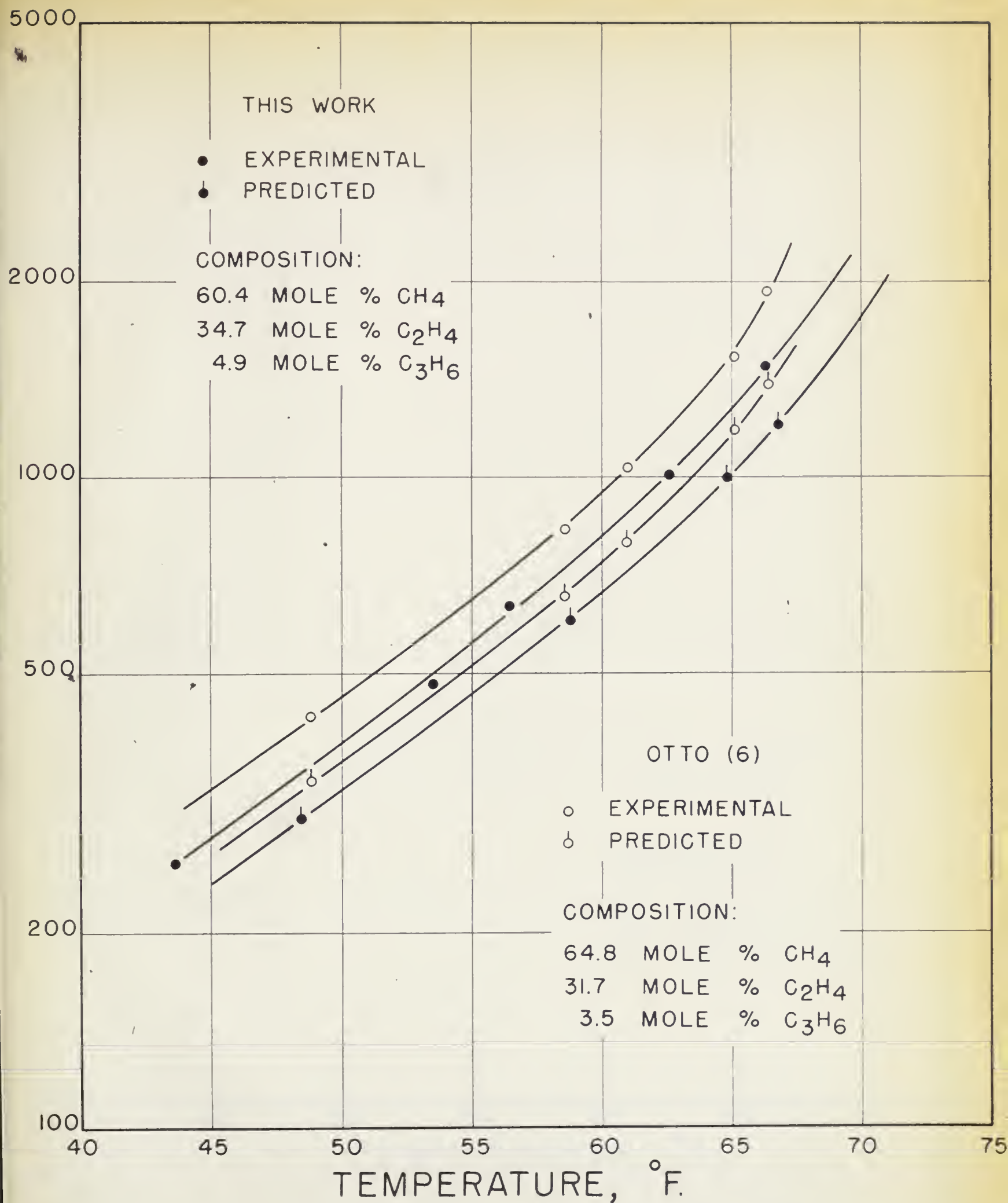


FIG. 16. COMPARISON OF CALCULATED WITH EXPERIMENTAL CONDITIONS FOR HYDRATE FORMATION

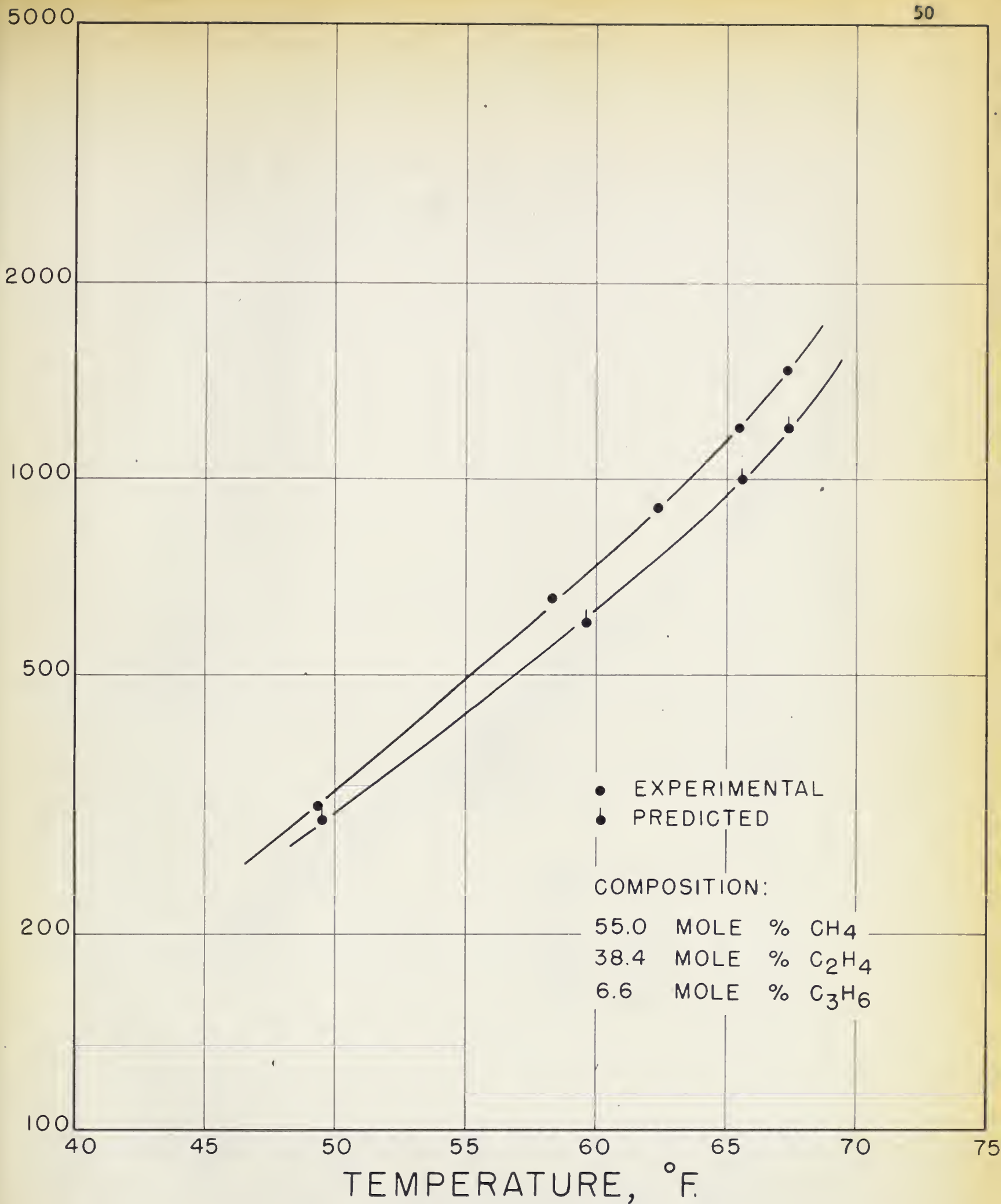


FIG. 17. COMPARISON OF CALCULATED WITH EXPERIMENTAL CONDITIONS FOR HYDRATE FORMATION

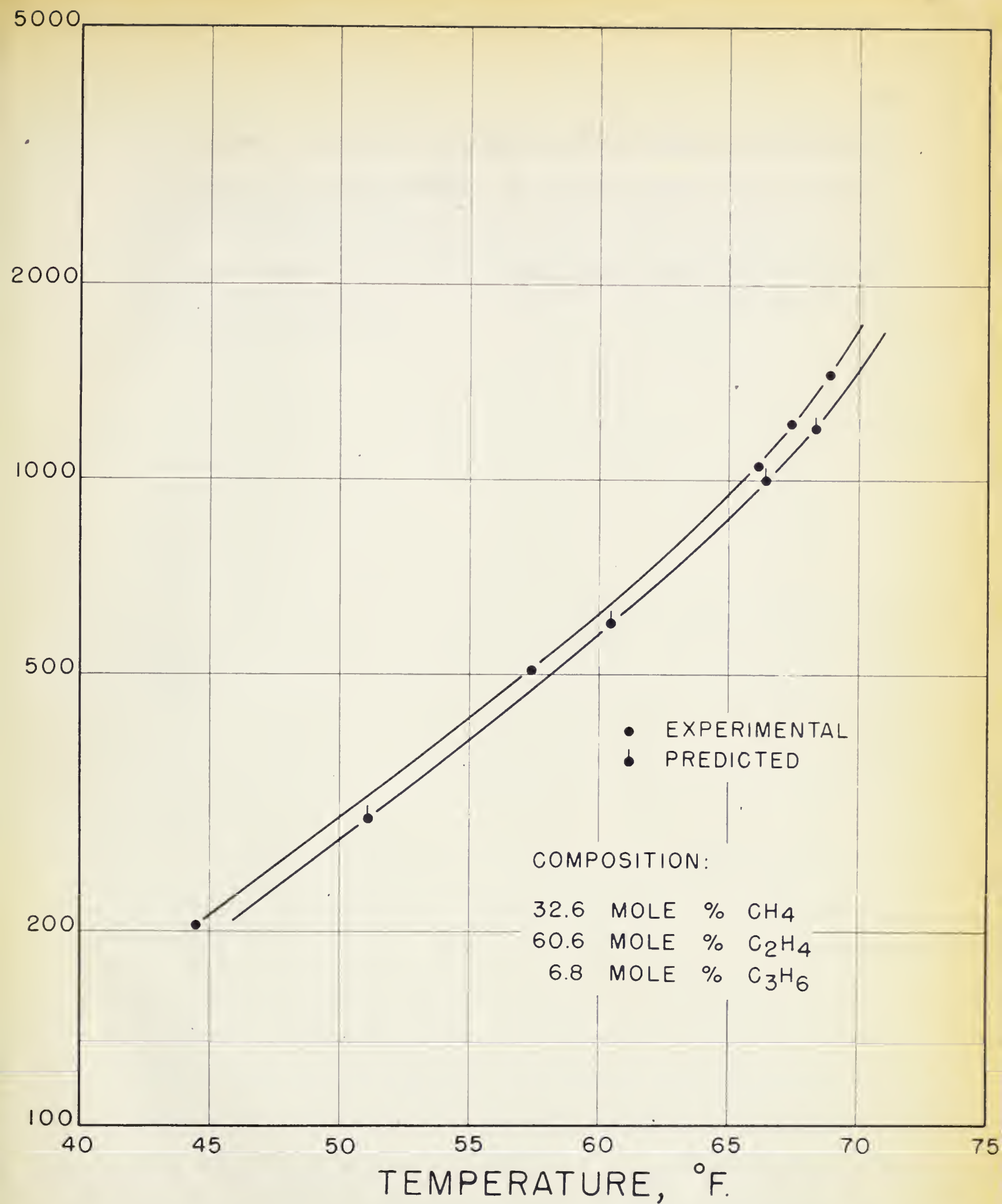


FIG. 18. COMPARISON OF CALCULATED WITH EXPERIMENTAL CONDITIONS FOR HYDRATE FORMATION

given pressure, this means that the calculated hydrate conditions will be higher than the experimental. It was found that as the percent of methane in the vapor increased, the percent deviation increased. The comparison between calculated and experimental conditions are shown in Table IX in the Appendix.

VI DISCUSSION

(1) Ethylene-Water System

As was mentioned previously, Otto (6) found that the slope of the equilibrium curve rose sharply at approximately 700 lb/in.²abs. and 62.9°F, and decreased again at approximately 1100 lb/in.²abs. and 64.9°F. It was also found in this work that the slope of this curve decreased and became relatively constant at 2500 lb/in.²abs. and 69.7°F. The slope then increased at 3500 lb/in.²abs. and 73.0°F but not as sharply as before. These phenomena of increasing and decreasing slopes seem to be peculiar to the ethylene-water system.

Villard (9) first noticed this phenomenon occurring and reported a critical decomposition temperature of 65.8°F. He felt that above this temperature, hydrate could not form no matter what the pressure. Otto extended the data to 2000 lb/in.²abs. and proved this postulate wrong. Further experimental data obtained in this work substantiated Otto's results.

Otto felt that this sharp increase in slope was due to the nearness of the liquid-vapor critical for pure ethylene which occurs at 748 lb/in.²abs. and 49.4°F. He felt that in this region it was possible for a phase, which was initially a gas at lower temperature, to be compressed to such a high density that the type of behavior associated with a liquid could be expected. Otto reasoned that the increase in slope of the curve representing the L₁HV equilibria in the ethylene-water system, is explained by the ethylene-rich phase assuming properties close to those of the ethane liquid and the effect of pressure on the

L₁HV equilibria is similar to the effect on the L₁L₂H equilibria in the ethane-water system. The effect of pressure on the L₁L₂H equilibria is much smaller than for the L₁HV equilibria and consequently the curve rises very quickly.

Another explanation of this sharp increase is by a phase change. On a pressure-temperature phase diagram, an inflection point in the curve indicates a first order phase transition. An example of a first order phase transition is the changing of a body centered cubic lattice to a face centered cubic lattice. This change in phase could be brought about by the addition or removal of water molecules in the crystal lattice and thus increasing or decreasing the number of molecules of water of hydration. Two inflections were noticed. The first at approximately 700 lb/in.²abs. and 62.9°F and the second at approximately 1100 lb/in.²abs. and 64.9°F. These two inflections are in the opposite direction to each other. That is, the first inflection increases the slope of the curve and the second decreases the slope of the curve. This would seem to indicate that in one case the crystal lattice is taking on more molecules of water and in the second case, tending to lose water molecules or vice-versa. A third inflection point was found to occur at approximately 3500 lb/in.²abs. and 73.0°F. This inflection was in the same direction as the lowest pressure inflection but not nearly as sharp. This means that some water molecules would be removed or added as in the first inflection but not the same amount.

(2) Methane-Ethylene-Water System

It was found for high ethylene concentrations in this system, that the three phase equilibria curve for L_1HV exhibited two inflection points similar to those for the three phase equilibria for the ethylene-water system. At lower ethylene concentrations, however, these curves were similar and parallel to the curve for the methane-water system. It would seem that the P-T plane of hydrate formation is reversing and eventually the ethylene hydrate will form at a lower temperature than the methane hydrate.

(3) Experimental Solid-Vapor Equilibrium Ratios

An attempt was made in this experimental work to obtain solid-vapor equilibrium ratios from experimental analysis only. This requires the formation of hydrate in equilibrium with water-rich liquid and vapor and the subsequent analysis for vapor and hydrate composition. As mentioned previously, this was attempted on two systems, methane-ethylene-water and methane-propylene-water.

With methane-ethylene-water, the first system tried, no consistent results could be obtained. It was found that the longer hydrate was allowed to form the higher would be the K value for methane and the lower for ethylene. This happens because the vapor phase composition is changing with time as hydrate forms. The ethylene in the vapor phase is depleted faster than the methane and therefore the K value for ethylene decreases. The system, methane-propylene-water, was next tried with the idea that if liquid propylene is present, the vapor composition would remain constant at a given pressure and temperature during the hydrate

formation. The solid-vapor equilibrium ratios for methane obtained using this system, were more consistent but were in error. It was felt that a true equilibrium was not being obtained. Another difficulty was in the liquid hydrocarbon phase disappearing and then the vapor composition would start to change and the same problem arose as with the methane-ethylene-water system.

(4) Methane-Ethylene-Propylene-Water System

The three phase equilibria L_1HV conditions were investigated for three compositions of this system and the predicted hydrate forming conditions were calculated. The error involved was from 1.7 to 3.9 percent in the temperature at a given pressure or about 20 to 25 percent error in the pressure at a given temperature.

It was found that as the methane concentration increased with a corresponding decrease in the ethylene and propylene, that the percent deviation increased.

These solid-vapor equilibrium ratios have been found to work quite well for natural gases but will not give an exact prediction.

VII FUTURE WORK

Future work might include the following:

- (i) A study of the methane-ethylene-water system investigated in this work at pressures greater than 5000 lb/in.²abs.
- (ii) A further attempt to obtain solid-vapor equilibrium ratios for methane, ethylene and propylene using the systems methane-ethylene-water and methane-propylene-water.
- (iii) Further experimental study of the system methane-ethylene-propylene-water and comparing with the calculated hydrate forming conditions with a view to improving K values.

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A P P E N D I X

TABLE V

EXPERIMENTAL HYDRATE FORMING CONDITIONS FOR

 $\text{CH}_4\text{-H}_2\text{O(H-L}_1\text{-V)}$ SYSTEM

<u>Pressure</u> <u>lbs/in² abs.</u>	<u>Temperature</u> <u>°F</u>
1257	52.7
1261	52.9
1690	57.4
2039	60.4
2916	65.4
3551	68.5
4143	70.1
4992	72.7

TABLE VI

EXPERIMENTAL HYDRATE FORMING CONDITIONS FOR

 $\text{C}_2\text{H}_4\text{-H}_2\text{O(H-L}_1\text{-V)}$ SYSTEM

<u>Pressure</u> <u>lbs/in² abs.</u>	<u>Temperature</u> <u>°F</u>
2137	68.8
2759	70.7
3114	71.9
3347	72.6
3499	73.2
3857	73.9
4144	74.4
4954	75.8

TABLE VII

EXPERIMENTAL HYDRATE FORMING CONDITIONS FOR

 $\text{CH}_4\text{-C}_2\text{H}_4\text{-H}_2\text{O(H-L}_1\text{-V)}$ SYSTEM

Pressure lbs/in ² abs.	Temperature °F	Mole % CH ₄ in Vapor (Dry Basis)	Mole % C ₂ H ₄ in Vapor (Dry Basis)
1231	56.4	95.3	4.7
2106	63.5		
3115	68.8		
4095	72.2		
4935	74.4		
1073	60.0	83.7	16.3
2061	67.7		
3125	72.0		
4103	75.2		
4985	77.6		
927	64.1	52.3	47.7
1574	70.4		
1720	71.0		
2104	72.4		
2580	74.4		
3168	76.2		
4098	78.8		
4896	81.3		
314	52.5	22.5	77.5
910	66.5		
1558	70.8		
2035	72.8		
3606	77.5		
4945	81.0		
332	53.4	7.6	92.4
831	65.3		
1534	69.8		
2138	71.8		
3495	75.3		
4956	78.8		

TABLE VIII

HYDRATE FORMING CONDITIONS FOR
 $\text{CH}_4\text{-C}_2\text{H}_4\text{-C}_3\text{H}_6\text{-H}_2\text{O(H-L}_1\text{-V) SYSTEM}$

<u>Pressure</u> <u>lbs/in² abs.</u>	<u>Temperature</u> <u>°F</u>	Gas Composition (Dry Basis)		
		<u>CH₄</u>	<u>C₂H₄</u>	<u>C₃H₆</u>
254	43.7	60.4	34.7	4.9
481	53.5			
636	56.5			
1016	62.6			
1495	66.3			
315	49.4	55.0	38.4	6.6
652	58.3			
905	62.4			
1197	65.5			
1488	67.4			
205	44.5	32.6	60.6	6.8
507	57.4			
1043	66.1			
1226	67.4			
1459	68.9			

TABLE IX

COMPARISON OF CALCULATED WITH EXPERIMENTAL
CONDITIONS FOR HYDRATE FORMATION

Pressure <u>lbs/in² abs.</u>	Hydrate Formation Temperature °F		Percent <u>Deviation</u>	Gas Composition Mole Percent (Dry Basis)		
	<u>Experimental</u>	<u>Calculated</u>		<u>CH₄</u>	<u>C₂H₄</u>	<u>C₃H₆</u>
300	50.1	51.2	2.19	32.6	60.6	6.8
600	59.6	60.5	1.51			
1000	65.6	66.5	1.37			
1200	67.3	68.5	1.78			
300	46.1	48.5	5.21	60.4	34.7	4.9
600	57.1	58.8	2.98			
1000	62.6	64.9	3.67			
1200	64.5	66.8	3.56			
300	48.7	49.5	1.65	55.0	38.4	6.6
600	57.5	59.7	3.83			
1000	63.5	65.7	3.47			
1200	65.4	67.4	3.06			

THE ANNUAL REPORT OF THE COMMISSIONER OF THE LAND OFFICE FOR THE YEAR 1890

<p>STATE OF</p> <p>NEW YORK</p>	<p>DEPARTMENT OF</p> <p>LAND OFFICE</p>	<p>COMMISSIONER</p> <p>OF THE</p> <p>LAND OFFICE</p>	<p>REPORT</p> <p>FOR THE YEAR</p> <p>1890</p>	<p>ALBANY:</p> <p>1891</p>
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<p>2. 1. 1. 1. 1.</p>	<p>2. 1. 1. 1. 1.</p>	<p>2. 1. 1. 1. 1.</p>	<p>2. 1. 1. 1. 1.</p>	<p>2. 1. 1. 1. 1.</p>
<p>3. 1. 1. 1. 1.</p>	<p>3. 1. 1. 1. 1.</p>	<p>3. 1. 1. 1. 1.</p>	<p>3. 1. 1. 1. 1.</p>	<p>3. 1. 1. 1. 1.</p>

TABLE X

CALIBRATION DATA FOR METHANE, ETHYLENE
AND PROPYLENE FOR KROMO-TOG

<u>Mole % CH₄</u>	<u>CH₄ Peak Height ins. x 200</u>	<u>Mole % C₂H₄</u>	<u>C₂H₄ Peak Height ins. x 200</u>	<u>Mole % C₃H₆</u>	<u>C₃H₆ Peak Height ins. x 200</u>
100	2132	100	1447	100	778
62.85	1450			37.15	358
53.72	1272	46.28	803		
32.48	811	33.78	628	33.74	356
		43.91	780	56.09	503

Sample Calculations

Prediction of Hydrate Formation

Component	Mole Fraction in the Gas (y)	K for the Component at 66°F and 1200 psia	y/K or x
CH ₄	0.604	1.18	0.512
C ₂ H ₄	0.347	0.861	0.403
C ₃ H ₆	<u>0.049</u>	0.401	<u>0.122</u>
	1.000		1.037

The assumed temperature of 66 °F is low, therefore try 67 °F

CH ₄	0.604	0.119	0.507
C ₂ H ₄	0.347	0.908	0.382
C ₃ H ₆	<u>0.049</u>	0.473	<u>0.103</u>
	1.000		.992

The assumed temperature of 67 °F is high, therefore
interpolation between 67 °F and 66 °F gives a value of
66.8 °F.

Therefore the equilibrium temperature at 1200 lb/in.² abs.
is 66.8 °F.

TABLE 1			
Summary of results of the survey			
Year	Number of respondents	Percentage of respondents	Percentage of total population
1950	100	100.0	100.0
1951	100	100.0	100.0
1952	100	100.0	100.0
1953	100	100.0	100.0
1954	100	100.0	100.0

TABLE 2			
Summary of results of the survey			
Year	Number of respondents	Percentage of respondents	Percentage of total population
1950	100	100.0	100.0
1951	100	100.0	100.0
1952	100	100.0	100.0
1953	100	100.0	100.0
1954	100	100.0	100.0

TABLE 3

Summary of results of the survey

TABLE 4

Summary of results of the survey

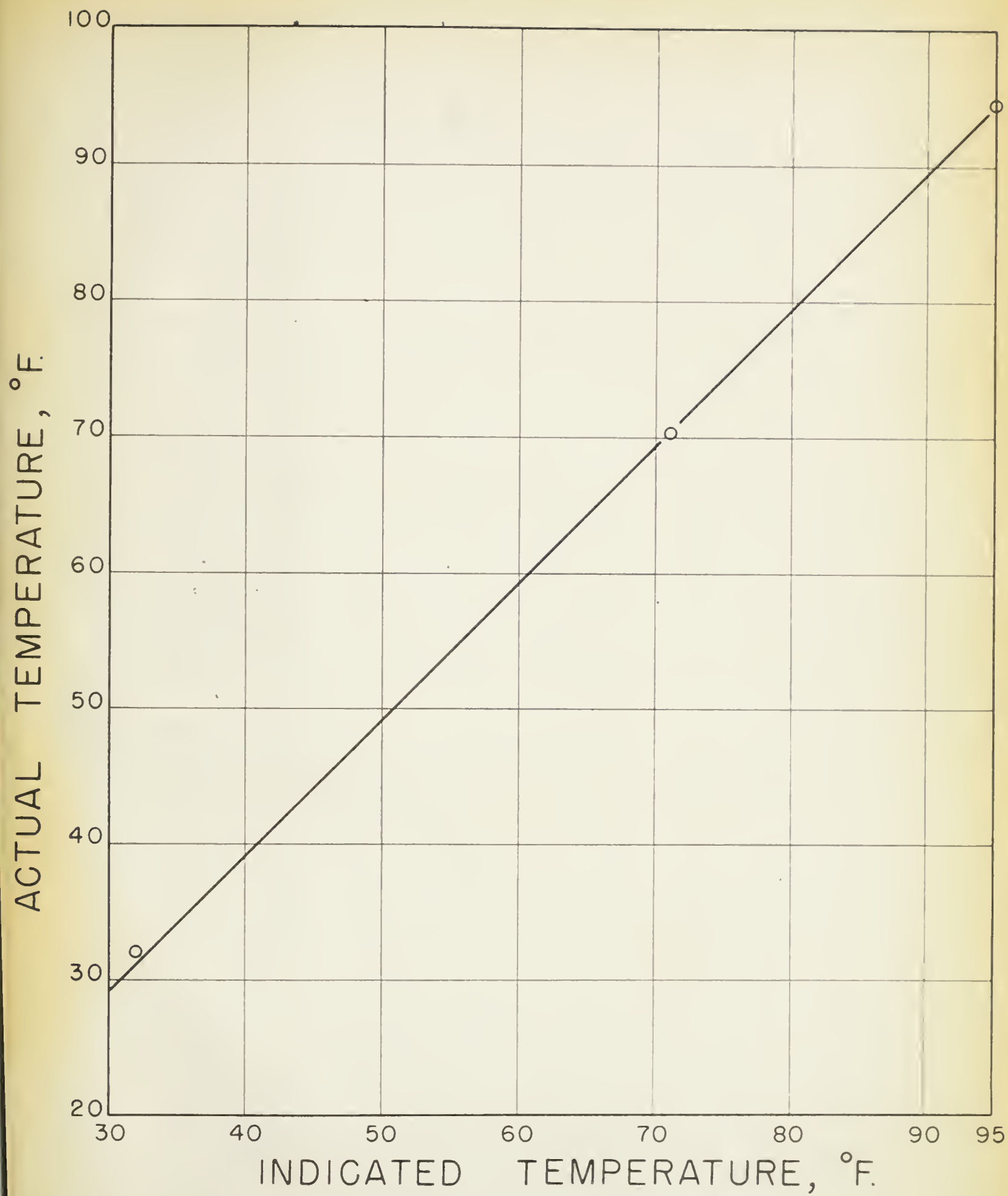
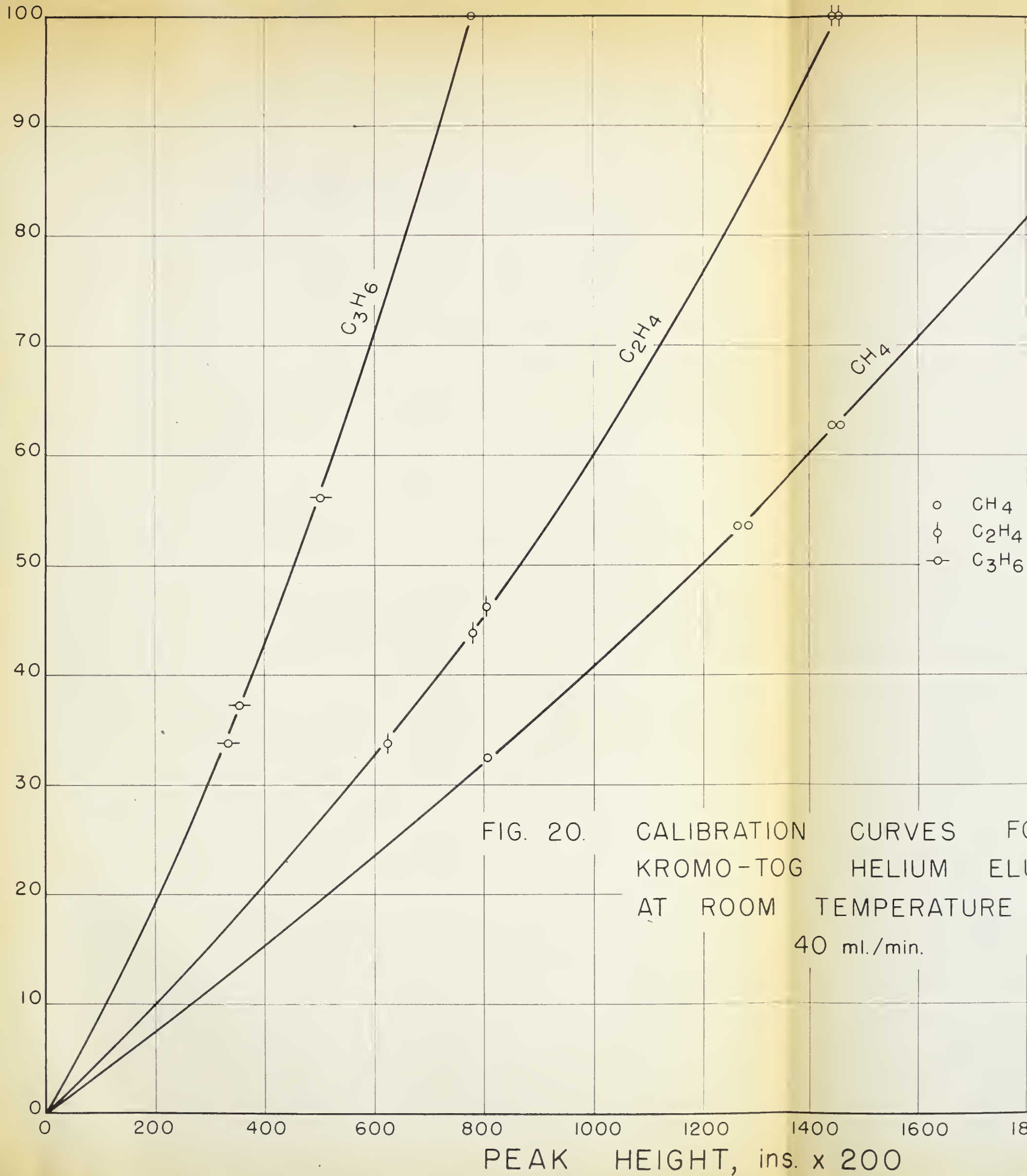
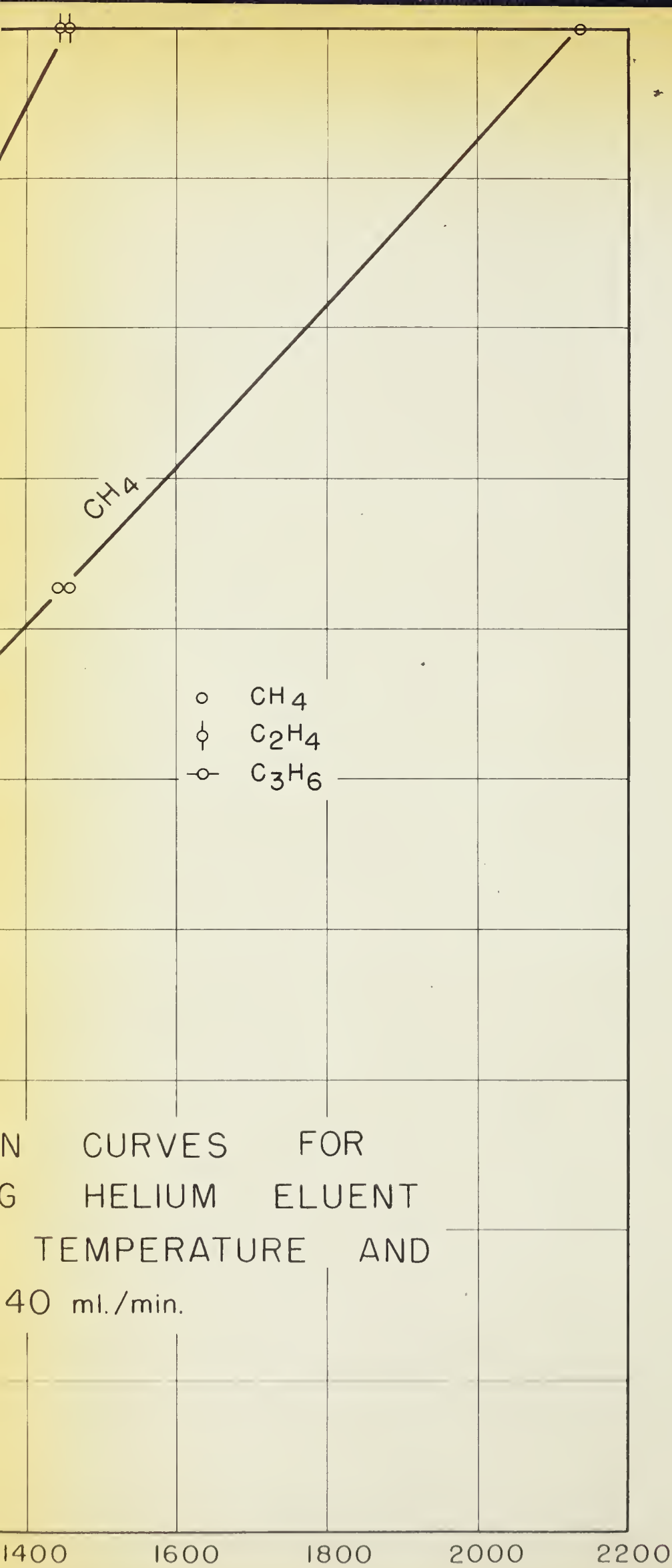


FIG. 19. THERMOCOUPLE CALIBRATION

MOLE PERCENT HYDROCARBON IN VAPOR





s. x 200



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